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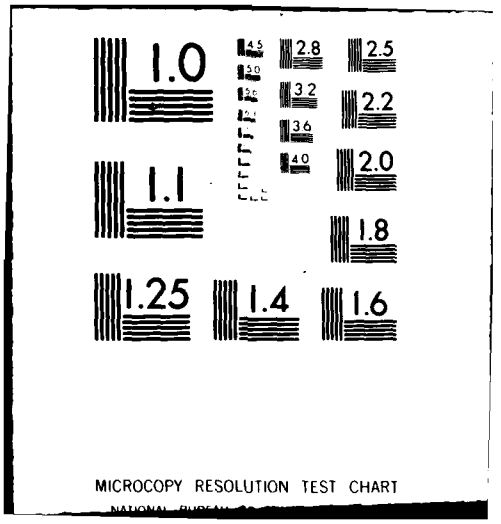
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Reactive flow systems often consist of multicomponent mixtures of neutral gases. Accurate modelling of reactive flows will, in many cases, require the accurate representation of transport phenomena in the conservation equations. In this paper, we identify and derive accurate, easy-to-evaluate equations for the coefficients of (ordinary) diffusion, viscosity, thermal conductivity, and thermal diffusion. The paper also serves to introduce and supplement the standard references on the subject for readers who are relatively new to the field.

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APPROXIMATE EQUATIONS FOR TRANSPORT COEFFICIENTS OF MULTICOMPONENT MIXTURES OF NEUTRAL GASES

I. Introduction

A description of multicomponent gas mixtures which contains the effects of fluid dynamics and chemical reactions is necessary for modelling many reactive flow systems. A quantitative description of such systems often must include an accurate treatment of transport phenomena, in which heat and particles diffuse through the mixture. Our particular interest in accurately modelling combustion processes has thus led us to survey and compare existing theories of transport phenomena in mixtures of neutral gases in order to identify representations which are suitable for numerical calculations. In this paper, we present the results of our work on (ordinary) diffusion, viscosity, thermal conductivity, and thermal diffusion.

To show how these transport processes enter our calculations, we consider the equations for conservation of mass, particle number, momentum, and energy, which may be written as follows:

$$\frac{\partial \rho}{\partial t} + \underline{\nabla} \cdot (\rho \underline{v}_0) = 0 \tag{I.1}$$

$$\frac{\partial n_i}{\partial t} = - \underline{\nabla} \cdot (n_i \underline{v}_0) - \underline{\nabla} \cdot (n_i \underline{\bar{V}}_i) + Q_i - L_i n_i \tag{I.2}$$

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$$\frac{\partial}{\partial t}(\rho \underline{v}_0) = -\underline{\nabla} \cdot (\rho \underline{v}_0 \underline{v}_0) - \underline{\nabla} \cdot \underline{\underline{P}} \tag{I.3}$$

$$\frac{\partial E}{\partial t} = -\underline{\nabla} \cdot (E\underline{v}_0) - \underline{\nabla} \cdot (\underline{v}_0 \cdot \underline{\underline{P}}) - \underline{\nabla} \cdot \underline{q} \tag{I.4}$$

Here $\underline{v}_0$ is the fluid velocity and $\rho, \rho\,\underline{v}_0$, and E are the total mass, momentum, and energy densities of the gas mixture, respectively. The sets of variables $\{n_i\}$, $\{Q_i\}$, and $\{L_i\}$ refer respectively to the number densities of the chemical species (labelled by i) and the rates of production and loss of the species as a result of chemical reactions. As we show in Appendix A, the transport coefficients enter the conservation equations through the pressure tensor $\underline{\underline{P}}$, the heat flux $\underline{q}$, and the diffusion velocities $\{\underline{\bar{v}}_i\}$, which represent the average velocities of the species relative to the fluid velocity, $\underline{v}_0$. The pressure tensor $\underline{\underline{P}}$ depends on the scalar pressure P and the viscosity of the mixture. The variables $\{\underline{\bar{v}}_i\}$ and $\underline{q}$ are functions of (ordinary) diffusion, thermal conductivity, and thermal diffusion. In Appendix A, we consider these relationships in detail.

The remaining sections of this paper present equations for the transport coefficients which represent the above processes in the conservation equations. In developing and identifying the formulas we have attempted to strike a balance between accuracy and computational simplicity. In the accompanying discussions, we have supplemented the major works on the theory of transport phenomena in gas mixtures[1,2] by citing publications which have extended the theory and by commenting on the consistency among and limitations of the various formulations. We have also sought to clarify points of confusion arising from differences in

methods of approximation and in notation used by various authors.

Because the text will often mention references 1 and 2, we will use the respective designations "HCB" and "CC" to identify them for the reader. We will employ the notation of HCB except when we are dealing with notational differences among authors and when we discuss vectors (e.g., $\underline{V}$), tensors (e.g., $\underline{\underline{B}}$), and the thermal diffusion coefficients $\{D_{Ti}\}$. In references to HCB and CC we cite the equation and page numbers, respectively, abbreviating the word "equation(s)" by "eq." (e.g., HCB,eq. (8.1-1), 516). We will express physical quantities in CGS units and will write units in parentheses beside the related definitions and equations.

II. Basic Formulations of the Theory of Transport Phenomena

Before stating the equations for transport coefficients in multicomponent gas mixtures, we will outline the approaches of HCB and CC in deriving the fundamental relations from which our equations originate. HCB and CC begin with the Boltzmann distribution functions $\{f_i\}$ which satisfy the Boltzmann equations for the species in the gas mixture:

$$\frac{\partial f_i}{\partial t} + (\underline{v}_i \cdot \frac{\partial f_i}{\partial \underline{r}}) + \frac{1}{m_i} (\underline{X}_i \cdot \frac{\partial f_i}{\partial \underline{v}_i}) = \sum_{j=1}^{\nu} J(f_i, f_j) \qquad (II.1)$$

$$(i = 1, 2, \ldots\ldots, \nu),$$

where f_i is a function of the position vector $\underline{r}$ (cm), the velocity vector of the i^{th} species $\underline{v}_i$ (cm sec^{-1}), and the time t(sec). The external force on each molecule of species i is $\underline{X}_i$ (dynes); the mass of a molecule of type i is m_i(g); the $\{J(f_i, f_j)\}$ are collision integrals; and ν is the number of species comprising the gas mixture. The authors assume that the $\{f_i\}$ may be expressed in terms of an infinite perturbation series

$$f_i = f_i^{[0]} + f_i^{[1]} + f_i^{[2]} + \ldots\ldots$$

$$(i = 1, 2, \ldots\ldots, \nu) \qquad (II.2)$$

where the lowest order term is Maxwellian, i.e.,

$$f_i^{[0]} = n_i \left(\frac{m_i}{2\pi kT} \right)^{3/2} \exp \left\{ \frac{-m_i (\underline{v}_i - \underline{v}_0)^2}{2kT} \right\}. \qquad (II.3)$$

In eq. (II.3), n_i is the number density of species i(cm^{-3}), k is

Boltzmann's constant (= 1.380662×10^{-16} erg $^{o}K^{-1}$); T is the temperature (^{o}K); and $\underline{v}_0(\underline{r},t)$ is the mass average (or fluid) velocity of the gas mixture given by

$$\underline{v}_0 (\underline{r},t) \equiv \frac{1}{\rho} \sum_{j=1}^{\nu} \rho_j \bar{\underline{v}}_j \qquad (\text{cm sec}^{-1}) \tag{II.4}$$

In eq. (II.4), $\rho(\underline{r},t)$ is the total mass density of the mixture and is equal to the sum of the species mass densities $\{\rho_i\}$:

$$\rho = \sum_{i=1}^{\nu} \rho_i \qquad (\text{gm cm}^{-3}), \tag{II.5}$$

where the individual mass densities ρ_i are given by

$$\rho_i = n_i m_i \quad (i = 1,2,\ldots,\nu). \tag{II.6}$$

Also in eq. (II.4) we have $\bar{\underline{v}}_i$, the average velocity of species i, defined by

$$\bar{\underline{v}}_i(\underline{r},t) = \frac{1}{n_i} \int f_i(\underline{r},\underline{v}_i,t)\, \underline{v}_i \, d\underline{v}_i \quad (\text{cm sec}^{-1}). \tag{II.7}$$

Given sufficiently rapid convergence of the series in eq. (II.2), we may use the first two terms to approximate f_i; HCB and CC use the following form:

$$f_i(\underline{r},\underline{v}_i,t) \cong f_i^{[0]} (\underline{r},\underline{v}_i,t) \{1+\phi_i (\underline{r},\underline{v}_i,t)\},$$

$$(i = 1,2,\ldots\nu), \tag{II.8}$$

where the function ϕ_i is found to be linear in $\nabla \ell n T$, the tensor $\nabla \underline{v}_0$ and a set of quantities $\{\underline{d}_j\}$, so that

$$\phi_i = -(\underline{A}_i \cdot \nabla \ell n T) - \sum_{\alpha,\beta=1}^{3} (\underline{B}_i)_{\alpha\beta} (\nabla \underline{v}_0)_{\beta\alpha} + n \sum_{j=1}^{\nu} \underline{C}_i^{(j)} \cdot \underline{d}_j \qquad \text{(II.9)}$$

$$(i = 1,2,\ldots,\nu).$$

In eq. (II.9), $\underline{A}_i$ and the set $\{\underline{C}_i^{(j)}\}$ are vectors, $\underline{B}_i$ is a second-rank tensor, and

$$\underline{d}_i = \nabla x_i + (x_i - \frac{\rho_i}{\rho}) \nabla P - \frac{\rho_i}{P\rho}\left[\frac{\rho}{m_i} \underline{X}_i - \sum_{j=1}^{\nu} n_j \underline{X}_j\right] \ (\text{cm}^{-1}) \qquad \text{(II.10)}$$

$$(i = 1,2,\ldots,\nu),$$

where P is the total scalar pressure, x_i is the mole fraction of species i given by

$$x_i = \frac{n_i}{n}, \qquad \text{(II.11)}$$

and n is the total number density equal to

$$n = \sum_{j=1}^{\nu} n_j. \qquad \text{(II.12)}$$

The quantities $\underline{A}_i$, $\underline{C}_i^{(j)}$, and $\underline{B}_i$ are all functions of the "peculiar velocity" $\underline{V}_i$, defined by

$$\underline{V}_i (\underline{r}, \underline{v}, t) \equiv \underline{v}_i - \underline{v}_0 \ (\text{cm sec}^{-1}) \qquad \text{(II.13)}$$

or, alternatively, the reduced velocity,

$$\underline{W}_i = \left(\frac{m_i}{2kT}\right)^{\frac{1}{2}} \underline{V}_i \qquad (\text{cm sec}^{-1}). \tag{II.14}$$

We then have

$$\underline{A}_i = A_i(W_i)\underline{W}_i, \tag{II.15}$$

$$\underline{C}_i^{(j)} = C_i^{(j)}(W_i)\ \underline{W}_i, \text{ and} \tag{II.16}$$

$$\underline{\underline{B}}_i = B_i(W_i)\ (\underline{W}_i\underline{W}_i - \tfrac{1}{3} W_i^2\ \underline{\underline{U}}) , \tag{II.17}$$

where the unit tensor is

$$\underline{\underline{U}} = \sum_{i=1}^{3} \underline{e}_i\underline{e}_i = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{II.18}$$

and

$$W_i = |\underline{W}_i|. \tag{II.19}$$

We must distinguish between the peculiar velocity $\underline{V}_i$ in eq. (II.13) and the "diffusion velocity" $\overline{\underline{V}}_i$, which is the <u>average</u> peculiar velocity of species i (i.e, the average rate of flow of species i relative to the mass average velocity of the mixture). Thus we have

$$\overline{\underline{V}}_i = \overline{\underline{v}}_i - \underline{v}_0 , \tag{II.20}$$

and, by eqs.(II.4) and (II.6), the set $\{\bar{V}_i\}$ satisfies the relation

$$\sum_{i=1}^{\nu} n_i m_i \bar{V}_i = \sum_{i=1}^{\nu} \rho_i \bar{V}_i = 0 \qquad \text{(II.21)}$$

From the above formalism, HCB and CC derive the transport coefficients in terms of integral equations containing $f_i^{[0]}$ and W_i along with A_i, $C_i^{(j)}$, or B_i depending on the particular transport coefficient being calculated. The approximate solution of these complicated equations requires two further steps:

(1) Expand the functions A_i, $C_i^{(j)}$ and B_i in terms of the Sonine polynomials $\{S_n^{(m)}(x)\}$, which satisfy a particularly convenient orthogonality condition(see Appendix B). This gives us the form:[3]

$$t_i^{(j)}(W_i) = \sum_m t_{im}^{(j)} S_n^{(m)}(W_i^2) \qquad \text{(II.22)}$$

where $t_i^{(j)}$ is equal to A_i, B_i, or $C_i^{(j)}$ and the number n is, respectively, 3/2, 5/2, or 3/2.

(2) Derive (integral) equations[4,5] satisfied by the sets $\{A_i\}$, $\{B_i\}$, and $\{C_i^{(j)}\}$ and use them in conjunction with (II.22) to solve for expansion coefficients $t_{im}^{(j)}$. These steps result in approximate equations for the transport coefficients in terms of a finite set of the $t_{im}^{(j)}$.

Unfortunately for the reader, HCB and CC calculate the expansion coefficients $t_{im}^{(j)}$ in different ways. To develop an "m^{th} order" approximation, HCB initially use expansions consisting of only the m lowest order Sonine polynomials, solving variationally for the coefficients. CC use expansions containing an infinite set of Sonine polynomials and develop expressions which may in theory be solved for the infinite set of coefficients. They then cut off the expansions at order m to obtain their "m^{th} - order" approximations for the transport coefficients. These techniques result in somewhat different equations at each order of approximation; however, we demonstrate later that, for most purposes, the differences are not significant.

The approximate equations for the mixture transport coefficients which are derived by HCB and CC take the form of ratios of determinants of order $\ell \geq \nu + 1$ and $\ell - 1$, respectively, where again ν is the number of species in the mixture. The elements of the determinants are complicated functions of collision integrals, the evaluation of which would require a significant amount of computer time. Consequently the expressions derived by HCB and CC are impractical for use in models of reactive flows. Subsequent work, however, has produced accurate, semi-empirical equations which are simple to evaluate. The remaining sections of this paper discuss these equations.

III. (Ordinary) Diffusion

A. Binary Mixtures (ν=2)

We will use the symbol $\mathcal{D}_{ij}$ to denote the "ordinary" (or"concentration") diffusion coefficient of a binary mixture containing species i and j. Marrero and Mason[6] have found that, for many binary mixtures of dilute gases, the existing experimental data are sufficiently extensive, consistent, and accurate to permit the development of a semi-empirical expression which describes the variation of $\mathcal{D}_{ij}$ over a wide temperature range($300^{\circ}K \leq T \leq 10000^{\circ}K$) and which has a standard deviation of 10% or less. Based on the qualitative temperature dependence of the quantity $P\mathcal{D}_{ij}$, where P is the pressure, Marrero and Mason used the following form to fit the more accurate and consistent data:

$$P\mathcal{D}_{ij}^{emp} = \frac{AT^{s}}{\{ \ln(\frac{\varphi_o}{kT}) \}^2 \exp (\frac{S}{T}) \exp (\frac{S'}{T^2})} \qquad \text{(III.1)}$$

where A, s, φ_o, S and S' are empirical constants. The empirical diffusion coefficient, $\mathcal{D}_{ij}^{emp}$, is in units of $cm^2\ sec^{-1}$, and P is in units of atmospheres.(One atmosphere equals 1.01325×10^6 dynes cm^{-2}.) The terms containing S and S' are the "Sutherland-Reinganum terms", which are used to account for the attractive portion of the intermolecular potential. Marrero and Mason fit most of the less precise data to the form

$$P\mathcal{D}_{ij}^{emp} = A'T^{s'} \qquad \text{(III.2)}$$

where A' and s' are empirical constants. The function in eq.(III.2) is much easier to evaluate and provides sufficient accuracy for reactive flow calculations. In those cases for which Marrero and Mason have fit the data to eq.(III.1), we suggest using eq.(III.1) to generate values of $P\mathcal{D}_{ij}$ at various temperatures and then fitting these to eq.(III.2).

For most intermediate or highly reactive species, experimental data do not exist over the large range of temperatures required for reactive flow calculations. We must then rely on a theoretical expression for $\mathcal{D}_{ij}$ which is based on kinetic theory. HCB and CC have derived the following equation for $[\mathcal{D}_{ij}]_1$, the first (or lowest nonzero order) approximation to $\mathcal{D}_{ij}$:[7]

$$[\mathcal{D}_{ij}]_1 = \frac{0.0026280}{P\sigma_{ij}^2\,\Omega_{ij}^{(1,1)*}(T_{ij}^*)} \sqrt{\frac{T^3(M_i + M_j)}{2\,M_i\,M_j}} \quad (cm^2\ sec^{-1}) \qquad \text{(III.3)}$$

where M_i is the molecular weight of species i, P is the pressure in atmospheres, and σ_{ij}, often called the collision diameter, is a force constant in the potential function

$$\phi_{ij} = \varepsilon_{ij}\, f\left(\frac{\sigma_{ij}}{r_{ij}}\right) \qquad \text{(III.4)}$$

which describes the interactions between molecules of species i and j. We may describe σ_{ij} as the value of the spherical coordinate r_{ij} at which ϕ_{ij} is equal to zero. The other constant, ε_{ij}, equals

the depth of the potential well(or the maximum energy of attraction). Unfortunately values of σ_{ij} and ϵ_{ij} are not available in most cases; so we will use the customary representations.

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j), \tag{III.5}$$

measured in $\overset{o}{A}$ ($1\overset{o}{A} = 10^{-8}$cm), and

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}\ , \tag{III.6}$$

measured in ergs. In eq.(III.5) and (III.6), the symbols σ_i and ϵ_i denote the force constants in eq. (III.4) for interactions between molecules of the same species i. Eq.(III.5) is exact for rigid spherical molecules while eq.(III.6) follows from the theory of the "London dispersion forces"[8].

Finally, the collision integral $\Omega_{ij}^{(1,1)^*}(T_{ij}^*)$, is actually a ratio[9]:

$$\Omega_{ij}^{(1,1)^*} = \frac{\Omega_{ij}^{(1,1)}}{[\Omega_{ij}^{(1,1)}]_{\text{Rigid Sphere}}} \approx 1 \tag{III.7}$$

where the collision integral $\Omega_{ij}^{(1,1)}$ is related to that defined in CC by

$$\Omega_{ij}^{(1,1)} = \Omega_{ij}^{(1)}(1). \tag{III.8}$$

Note that $\Omega_{ij}^{(1,1)^*}$ measures the departure of $\Omega_{ij}^{(1,1)}$ from its value in a model assuming rigid spherical molecules. The collision integral is a function of a reduced temperature

$$T_{ij}^{*} = \frac{kT}{\epsilon_{ij}} \quad . \tag{III.9}$$

To obtain values of ϵ_{ij} and σ_{ij} we suggest using the tabulations of ϵ_i and σ_i given by Svehla[10] and HCB[11] for interactions described by the Lennard-Jones potential,

$$\Phi_{LJ}(r) = 4\epsilon_i\left[\left(\frac{\sigma_i}{r}\right)^{12} - \left(\frac{\sigma_i}{r}\right)^{6}\right] \tag{III.10}$$

HCB[12] also provide a table of collision integrals $\Omega^{(\ell,s)^*}$ for small values of ℓ and s. Table III-1 compares values for $\mathcal{D}_{ij}$ calculated from the semiempirical formulas of Marrero and Mason with those calculated from eq (III.3-10). At low temperatures the agreement is quite good; however, the disparity increases with temperature. As in the case of eq. (III.1), we may transform eq.(III.3) to the form of eq.(III.2) by using eq.(III.3) to generate values of $P\mathcal{D}_{ij}$ at various temperatures and then fitting these values to eq.(III.2).

Based on the assumption of rigid spherical molecules, Cheung et al.[13] and Mason and Saxena[14] have derived an approximate equation for $\mathcal{D}_{ij}$ for mixtures of nonpolar gases:

$$\begin{aligned}\frac{\mathcal{D}_{ii}}{\mathcal{D}_{ik}} &\simeq \frac{1}{2\sqrt{2}}\left(1 + \frac{M_i}{M_k}\right)^{-1/2}\left[1 + \left(\frac{\lambda_i^o}{\lambda_k^o}\right)^{1/2}\left(\frac{M_i}{M_k}\right)^{1/4}\right]^2 \\ &= \frac{1}{2\sqrt{2}}\left(1 + \frac{M_i}{M_k}\right)^{-1/2}\left[1 + \left(\frac{\eta_i}{\eta_k}\right)^{1/2}\left(\frac{M_k}{M_i}\right)^{1/4}\right]^2 \\ &= \phi_{ik}\end{aligned} \tag{III.11}$$

Table III-1

Comparison of Theoretical and Empirical Values of

Binary Diffusion Coefficients at 1 Atm.

GAS MIXTURE	FORCE CONSTANTS[10] σ_{ij}(Å)	ε_{ij}/k (°K)	TEMPERATURE (°K)	$\Omega^{(1,1)*}_{ij}$	$[\mathcal{D}_{ij}]_1$ {eq.(III.3)} ($cm^2\ sec^{-1}$)	$\mathcal{D}^{emp}_{ij}$ ($cm^2 sec^{-1}$)
He - O_2	3.009	33.02	300	0.7545	0.7496	0.7522
			1500	0.5849	10.81	11.79
			3000	0.5249	34.08	38.58
H_2-O_2	3.147	79.81	300	0.8965	0.7927	0.8138
			1500	0.6735	11.80	13.22
			3000	0.6026	37.29	43.90
Ar - N_2	3.670	81.62	300	0.9013	0.1960	0.1977
			1500	0.6767	2.919	3.317
			3000	0.6048	9.236	11.17

In eq. (III.11), λ_i^0 (erg cm^{-1} sec^{-1} $^oK^{-1}$) is the coefficient of thermal conductivity calculated for a gas consisting only of species i at the same pressure and temperature as the mixture being studied ($T_i = T_{mix}$, $P_i = P_{mix}$) and with the internal degrees of freedom "frozen". The last condition means that species i is treated as a monatomic gas when determining λ_i^o (Section V). Similarly, η_i (gm cm^{-1} sec^{-1}) is the coefficient of viscosity of a gas consisting of only species i at the same temperature and pressure as the mixture being studied (Section IV). The quantity $\mathcal{D}_{ii}$ is the coefficient of "self-diffusion", for which we can use the first approximation,[15]

$$\mathcal{D}_{ii}]_1 = \frac{0.0026280}{P\sigma_i^2 \Omega_{ii}^{(1,1)*}(T_i^*)} \sqrt{\frac{T^3}{M_i}} \quad (cm^2\ sec^{-1}), \qquad \text{(III.12)}$$

where all quantities are defined as in the case of eq. (III.3) and we have substituted σ_i and T_i^* for σ_{ii} and T_{ii}^*, respectively. In eq. (IV.10) we also present a semi-empirical expression for $\mathcal{D}_{ii}$. Table III-2 compares experimental values of $\mathcal{D}_{ii}$ with those calculated from eq. (III.12). Again the agreement is quite good.

TABLE III-2*

Comparison of Theoretical and Experimental Values of

Self-Diffusion Coefficients at 1 Atm.

GAS	FORCE CONSTANTS[10]		TEMPERATURE(°K)	$\Omega_{ii}^{(1,1)}$*	$[\mathscr{D}_{ii}]_1$(eq.III.12) (cm^2 sec^{-1})*	$\mathscr{D}_{ii}$ (experimental) (cm^2 sec^{-1})[16]
	σ (Å)	ε/k (°K)				
Ne	2.820	32.8	77.7	1.016	0.0498	0.0492
			273.2	0.7661	0.436	0.452
			353.2	0.7364	0.666	0.703
N_2	3.798	71.4	77.7	1.382	0.0171	0.0168
			273.2	0.8928	0.174	0.185
			353.2	0.8440	0.271	0.287
O_2	3.467	106.7	77.7	1.694	0.0156	0.0153
			273.2	0.9925	0.176	0.187
			353.2	0.9249	0.277	0.301

* After HCB, Table 8.4-13, 581.

Cheung et al,[12] have shown that the ϕ_{ij} calculated from eq.(III.11) using experimentally determined viscosity coefficients agrees quite well with the ratio $\mathcal{D}_{ii}/\mathcal{D}_{ij}$ calculated from eqs.(III.3) and (III.12) using a Lennard-Jones potential. Discrepencies will, however, arise because the derivation of eq. (III.11) relies on the assumption of rigid sperical molecules.

B. Multicomponent Mixtures ($\nu > 2$)

The calculation of diffusion coefficients (denoted D_{ij} as opposed to $\mathcal{D}_{ij}$) for mixtures of more than two species requires the evaluation of determinants of order ν and the associated minors.[17,18] For more than four species, the calculation of the set $\{D_{ij}\}$ could become expensive; fortunately, both HCB and CC have derived expressions relating ordinary diffusion to other transport properties in terms of $[\mathcal{D}_{ij}]_1$ the first approximation to the binary diffusion coefficient given in eq.(III.3). We mention that, while $[\mathcal{D}_{ij}]_1$ is the same in the formulations of HCB and CC, the first approximation to D_{ij} (denoted $[D_{ij}]_1$) is not. We infer this from the fact that [19]

$$[D_{ij}]_1^{CC} \equiv [\mathcal{D}_{ij}]_1 \qquad \text{(III.13)}$$

while eq.(III.13) does not hold in the case of HCB.[17] Thus we have

$$[D_{ij}]_1^{HCB} \neq [D_{ij}]_1^{CC} , \qquad \text{(III.14)}$$

a situation which we also find for coefficients of thermal diffusion (Section VI).

From a practical point of view, the above disagreement between the theoretical formulations may not be too significant. Marrero and Mason[6] point out that the major difference between D_{ij} and $\mathcal{D}_{ij}$ lies in the dependence of D_{ij} on the relative amounts of all species rather than just species i and j as in the case of $\mathcal{D}_{ij}$. Because the experimental uncertainties in measurements of D_{ij} and $\mathcal{D}_{ij}$ are often of the same order of magnitude as the variations in composition, Marrero and Mason suggest that

$$D_{ij}^{emp} \simeq \mathcal{D}_{ij}^{emp} , \qquad \text{(III.15)}$$

where "emp" signifies empirically determined quantities.

C. Summary

From the above discussions, we find that good experimental data and simple empirical formulas exist for binary diffusion coefficients of many species. For those which are not adequately covered by measurements, we may use either eq. (III.3)or the combination of eqs. (III.11) and (III.12). Because HCB and CC have constructed the equations describing diffusion and other transport phenomena in terms of the binary diffusion coefficients, we need not calculate the multicomponent coefficients of diffusion, which are defined differently by HCB and CC.

IV. Viscosity

A. Pure Gas

For a pure gas (i.e., one which contains only one species), we may calculate the coefficient of viscosity, η_i, by using the expression[20]

$$[\eta_i]_1 = \frac{266.93 \times 10^{-7} \sqrt{M_i T}}{\sigma_i^2 \, \Omega_{ii}^{(2,2)*}(T_i^*)} \quad (\text{g cm}^{-1} \text{ sec}^{-1}) \tag{IV.1}$$

where $[\eta_i]_1$ denotes the first (i.e., lowest nonzero order) approximation to η_i. In eq. (IV.1), $\Omega_{ii}^{(2,2)*}$ is a ratio of collision integrals[9] defined by

$$\Omega_{ii}^{(2,2)*} \equiv \frac{\Omega_{ii}^{(2,2)}}{[\Omega_{ii}^{(2,2)}]_{\text{Rigid-Sphere}}} \approx 1 \tag{IV.2}$$

where the collision integral $\Omega_{ii}^{(2,2)}$ is related to that defined in CC by

$$\Omega_{ii}^{(2,2)} = \Omega_{ii}^{(2)}(2). \tag{IV.3}$$

HCB[21] have compared experimental viscosity data with values calculated from eq. (IV.1) and eq. (III.10) for several species over a temperature range of 80 - 1500°K and have found deviations of less that 5% in all cases. For sufficiently restricted temperature ranges we might simplify the calculations by substituting a constant for $\Omega_{ii}^{(2,2)*}$, which is a slowly varying function of reduced temperature T^*. As we showed in eq. (III.11), $[\eta_i]_1$ and $[\lambda_i^o]_1$ are closely related; we will show this relationship explicitly in Section V.

B. Multicomponent Mixtures ($\nu \geq 2$)

For mixtures of two or more gases, we may express the first approximation to the coefficient of viscosity, $[\eta_{mix}]_1$, as a ratio of determinants of order $\nu + 1$ and ν, respectively, in which the elements are complicated functions of collision integrals.[22] Of more use in reactive flow calculations is an alternate expression derived by expanding the determinants and discarding the off-diagonal elements. This results in the functional form[23]

$$[\eta_{mix}]_1 \simeq \sum_{i=1}^{\nu} \frac{x_i^2}{\frac{x_i^2}{[\eta_i]_1} + \sum_{\substack{k=1 \\ k\neq i}}^{\nu} \alpha_o \, x_i x_k \frac{RT}{PM_i [\mathscr{D}_{ik}]_1}}$$

$$= \sum_{i=1}^{\nu} \frac{[\eta_i]_1}{1 + \alpha_o \frac{[\eta_i]_1 \, RT}{x_i \, PM_i} \sum_{\substack{k=1 \\ k\neq i}}^{\nu} \frac{x_k}{[\mathscr{D}_{ik}]_1}} \quad , \tag{IV.4}$$

where $[\eta_i]_1$ is the first approximation to the coefficient of viscosity of a gas containing only species i at the temperature and pressure of the mixture being studied, α_o is an empirical constant, and R is the "molar gas constant" given by

$$R = \tilde{N}k = 8.31441 \times 10^{7} \text{ erg mol}^{-1} \, {}^{o}K^{-1} \tag{IV.5}$$

with Avogadro's number given by

$$\tilde{N} = 6.022045 \times 10^{23} \text{ mol}^{-1} \quad . \tag{IV.6}$$

We may also express eq. (IV.4) in terms of ρ_i', the density (g cm^{-3}) of a gas containing only species i at the temperature and pressure of the mixture, by using the ideal gas law:

$$PV = \tau_i RT. \tag{IV.7}$$

Here τ_i is the number of moles of a gas containing only species i at the same temperature and pressure as the mixture (and not the number of moles of species i in the mixture). We then obtain

$$[\eta_{mix}]_1 \cong \sum_{i=1}^{\nu} \frac{[\eta_i]_1}{1 + \frac{\alpha_o [\eta_i]_1}{\rho_i' x_i} \sum_{\substack{k=1 \\ k \neq i}}^{\nu} \frac{x_k}{[\mathscr{D}_{ik}]_1}} \tag{IV.8}$$

We point out again that ρ_i' is not the density of species i in the mixture; rather ρ_i' is the density corresponding to τ_i in eq. (IV.7). Using a heuristic treatment, Buddenberg and Wilke[24] obtained eq. (IV.8) with η_{mix} and η_i substituted for $[\eta_{mix}]_1$ and $[\eta_i]_1$ and evaluated α_o to be approximately 1.385 by comparing (IV.8) with available viscosity data for binary mixtures. Table IV-1 shows that we can calculate values of η_{mix} which are in excellent agreement with experimental data for mixtures of two, three, and four components by using eq. (IV.8) with $\alpha_o = 1.385$ and experimental values of ρ_i' and η_i. The dependence of eq. (IV.8) on binary diffusion coefficients, for which data are often unavailable, can make calculations of mixture viscosities more difficult and less accurate. Wilke[25], therefore, developed the following equation for $[\eta_{mix}]_1$ in terms of the quantities $\{\phi_{ik}\}$, defined by eq. (III.11):

Table IV-1*

Comparison of Theoretical and Experimental Values of Viscosity Coefficients of Gas Mixtures at 298°K and 1 Atmosphere

Gas Mixture	Mole Fractions	η_{mix} (Experimental)[26] 10^{-6} g cm^{-1} sec^{-1}	η_{mix} (Theoretical) 10^{-6} g cm^{-1} sec^{-1}	
N_2-O_2	0.1864-0.8136	200.8	197.4 [24,a]	
	0.7822-0.2178	184.3	180.6 [24,a]	
H_2-CO	0.1927-0.8073	171.7	171.9 [24,a]	
	0.6947-0.3053	144.9	149.6 [24,a]	
He-Ar	0.3405-0.6595	227.8	227.0 [24,a]	
	0.7565-0.2435	227.0	227.8 [24,a]	
Ne-H_2-CO_2	0.333-0.333-0.333	185.7	195.3 [24,a]	190.2 [25,b]
Ne-H_2-CO_2 -CCl_2F_2	0.25-0.25-0.25-0.25	168.1	162.3 [24,a]	159.3 [25,b]

* After Buddenberg and Wilke. [24]

a. From eq. (IV.8) of this paper.

b. From eq. (IV.9) of this paper.

$$\eta_{mix} \simeq \sum_{i=1}^{\nu} \frac{\eta_i}{1 + \frac{1}{x_i} \sum_{\substack{k=1 \\ k\neq i}}^{\nu} x_k \phi_{ik}} \qquad \text{(IV.9)}$$

$$= \sum_{i=1}^{\nu} \frac{\eta_i}{\sum_{k=1}^{\nu} \frac{x_k}{x_i} \phi_{ik}} \,.$$

Using eq. (III.11), (IV.8), and (IV.9) we may derive a simple approximate formula for $\mathscr{D}_{ii}$, the coefficient of self diffusion:

$$\mathscr{D}_{ii} \simeq 1.385 \frac{\eta_i}{\rho_i} \,. \qquad \text{(IV.10)}$$

Table IV-1 shows that eq. (IV.9), when used with experimental values of η_i will give excellent agreement with experimental data for mixtures of up to four components. We also note that eq. (IV.9) has some advantages over eq. (IV.8) because ϕ_{ik} depends only on the molecular weights and the viscosities of the individual components. By eq. (IV.1), we have

$$\frac{\eta_i}{\eta_k} \simeq \left(\frac{M_i}{M_k}\right)^{\frac{1}{2}} \frac{\sigma_k^2}{\sigma_i^2} \frac{\Omega_{kk}^{(2,2)*}(T_k^*)}{\Omega_{ii}^{(2,2)*}(T_i^*)} \qquad \text{(IV.11)}$$

and from eq. (III.11) and eq.(IV.11), we obtain

$$\phi_{ik} \simeq \frac{1}{2\sqrt{2}} \left(1 + \frac{M_i}{M_k}\right)^{-\frac{1}{2}} \left[1 + \frac{\sigma_k}{\sigma_i} \left\{ \frac{\Omega_{kk}^{(2,2)*}(T_k^*)}{\Omega_{ii}^{(2,2)*}(T_i^*)} \right\}^{\frac{1}{2}} \right]^2 \qquad \text{(IV.12)}$$

Depending on the species in the mixture and the size of the reduced temperature range of interest (T_A^*, T_B^*), we might simplify eq. IV. 12 by replacing

$$Z_{ki} \equiv \left[\frac{\Omega_{kk}^{(2,2)*}(T_k^*)}{\Omega_{ii}^{(2,2)*}(T_i^*)} \right]^{1/2} \qquad \text{(IV.13)}$$

with its average over (T_A^*, T_B^*). For models involving a large range of reduced temperatures, accurate calculations will require the use of a Table of $\Omega^{(2,2)*}$ values vs. T^* or an accurate fit of a convenient functional form to the tabulated values.

V. Thermal Conductivity

The expression for the coefficient of thermal conductivity for a mixture of reacting gases, λ_{mix}, is often quite complex, as we indicate in Appendices A, D, and E. Depending on the speeds of the reactions and on the lifetimes of the excited states of each molecule, we may express λ_{mix} as follows:

$$\lambda_{mix} = \lambda^{\circ}_{mix} + \lambda^{int}_{mix} + \lambda^{comp}_{mix}. \qquad (V.1)$$

In eq.(V.1), λ°_{mix} (sometimes called the "translational thermal conductivity") is a function of the set $\{\lambda^{\circ}_i \mid i=1,2,\ldots,\nu\}$ of thermal conductivities of the individual species, each treated as monatomic. The *second term*, λ^{int}_{mix}, accounts for the transport of internal energy by molecules in different quantum states, and the last term, λ^{comp}_{mix}, describes heat conduction resulting from changes in the composition of the mixture through chemical reactions. We must point out, however, that the heat flux resulting from changes in chemical composition of the mixture may be represented as

$$\underline{q}^{comp} = - \lambda^{comp}_{mix} \nabla T \qquad (V.2)$$

<u>only</u> if the steady state chemical composition is very nearly in equilibrium with the local temperature T. Because this depends on the reaction rates in the forward and reverse directions, the term λ^{comp}_{mix} in eq.(V.1-2) is not always applicable. We have, therefore, derived the following general expression for $\underline{q}^{comp}$ in Appendix **D**:

$$\underline{q}^{comp} = \sum_{i=1}^{\nu} \mathcal{N} x_i \bar{\underline{V}}_i \langle H_i \rangle, \qquad (V.3)$$

where $\mathcal{N}$ is the number of moles in the gas mixture and $\langle H_i \rangle$ is the experimentally determined enthalpy per mole of gas species i. We may now restate eq.(V.1) as

$$\lambda_{mix} = \lambda^{o}_{mix} + \lambda^{int}_{mix} \quad . \qquad (V.4)$$

In the remaining sections, we will discuss λ^{o}_{mix} and λ^{int}_{mix} in detail.

A. Pure Gas

For a gas consisting of only one species, we first consider λ^{o}_{i}, which is calculated assuming that the gas is monatomic or that the internal degrees of freedom are frozen. HCB[27] give the following expression for the first approximation, $[\lambda^{o}_{i}]_1$:

$$[\lambda^{o}_{i}]_1 = \frac{8.322 \times 10^{3}}{\sigma_i^2 \, \Omega^{(2,2)*}_{ii}(T^{*}_{i})} \left(\frac{T}{M_i} \right)^{1/2} (\text{erg cm}^{-1} \text{ sec}^{-1} {}^{o}\text{K}^{-1}). \qquad (V.5)$$

By eq.(IV.1) and eq.(V.5), we find that $[\eta_i]_1$ and $[\lambda^{o}_{i}]_1$ are clsoely related, i.e.

$$[\eta_i]_1 = 3.208 \times 10^{-9} \, M_i [\lambda^{o}_{i}]_1 . \qquad (V.6)$$

For polyatomic molecules, of course, the internal degrees of freedom are not frozen, and the diffusion of molecules of species i in different quantum states will transport energy through the gas. We may represent this process approximately by using the Eucken factor,[27] E_i, with eq.(V.5) as follows :

$$\lambda_i = \lambda_i^o + \lambda_i^{int} = \lambda_i^o E_i \ . \qquad (V.7)$$

Hirschefelder[28-31] has derived the following equation for E_i from the kinetic theory of gases (Appendix E):

$$E_i = 0.115 + 0.354 \ \frac{c_{pi}}{R} \qquad (V.8)$$

$$= 0.115 + 0.354 \ \frac{\gamma_i}{\gamma_i - 1} \ ,$$

where c_{pi} is the constant pressure molar specific heat for molecular species i,

$$\gamma_i = \frac{c_{pi}}{c_{vi}} \ , \qquad (V.9)$$

and c_{vi} is the constant volume molar specific heat for molecular species i.

Hirschfelder assumed the following in order to derive eq.(V.8):

(1) The gas exists in a steady state.

(2) The composition of the gas (i.e., population of the various quantum levels) is in equilibrium with the local temperature. Only when this assumption holds will the heat conductivity be independent of boundary conditions, permitting us to express the heat flux due to internal degrees of freedom as

$$\underline{q}_i^{int} = - \lambda_i^{int} \ \underline{\nabla} T \ . \qquad (V.10)$$

If, for example, an appreciable fraction of the molecules were to exist

in metastable states, the population of states would not be a function temperature only. Eq. (V.10) would then be incorrect and λ_i^{int} would not provide a meaningful representation of polyatomic effects.

(3) The coefficients of diffusion for all quantum states with a nonnegligible population are approximately the same. This is usually the case, except when excited electronic states are appreciably populated. Such states have collision diameters σ_i^α which are on the order of $3\sigma_i^\circ$, where α is the label of the quantum state and $\alpha = 0$ signifies the ground state. The large values of σ^α for excited electronic states result in much smaller diffusion coefficients, which vary as $(\sigma^\alpha)^{-2}$, than for the ground electronic state, and consequently the Eucken factor would predict a λ_i which is larger than the experimental data would indicate.

(4) Nonadiabatic collisions do not appreciably distort the molecular distribution functions $\{f_i^\alpha (\underline{r}, \underline{v}_i^\alpha, t) \mid \alpha = 0,1,2,....\}$ for the various quantum species α. This holds in the case of electronic and vibrational states. However, at "low" temperatures, where rotational transitions become important in collisional energy transfer, rather large distortions do occur in the distribution functions, leading to anomalously small experimental values of λ_i. For nonpolar molecules, "low temperature" means $\sim 170^\circ K$, while for polar molecules, "low temperature" signifies room temperature. Fortunately the Eucken factor works well at higher temperatures which are of interest in reactive flow problems, because the distortions due to rotational transitions are less important.

Appendix E shows how these assumptions are used to derive E_i. Subsequent work[32-34] has accounted for the effects of the inelastic collisions mentioned above and has resulted in an Eucken type factor which involves

only measurable quantities plus the relaxation time associated with the transfer of energy due rotational transitions in collisions. CC[35] indicate that these results are highly model dependent and are currently impractical for application to reactive flow calculations.

B. Multicomponent Mixtures ($\nu \geq 2$)

HCB[36] derive $[\lambda^{\circ}_{mix}]_1$, the first approximation to λ_{mix} for monatomic gases, in terms of a ratio of determinants of orders $2\nu + 1$ and 2ν, respectively, plus a term involving thermal diffusion and ordinary diffusion coefficients. Subsequent work[37-41] has led to a simpler equation involving only a ratio of determinants of order $\nu + 1$ and ν, respectively. As we indicated in Section II, the "first approximation", $[\lambda^{\circ}_{mix}]_1$, differs from author to author because different methods of approximation have been used. Mason[37] used Kihara's method,[42] in which derivatives with respect to temperature of a particular set of functions of collision integrals $\Omega^{(\ell,s)}_{ij}$ are discarded. Muckenfuss and Curtiss[39] used the variational equations of HCB, and CC[41] used truncation of an infinite series expansion to develop a set of ν coupled equations for $[\lambda^{\circ}_{mix(i)}]_1$, where

$$[\lambda^{\circ}_{mix}]_1 \equiv \sum_{i=1}^{\nu} [\lambda^{\circ}_{mix(i)}]_1. \qquad (V.11)$$

We show in Appendix C that the equations of CC lead to a ratio of determinants of orders $\nu + 1$ and ν, respectively, with elements that differ only slightly from those of Mason[37] and Muckenfuss and Curtiss.[39] Unfortunately the above formulas depend on functions of collision integrals which are nonlinear functions of temperature.

Subsequently Mason et al.[14,43] have found that the off-diagonal elements of the determinants could be neglected and that the portion of the diagonal elements which contains the collision integrals could be replaced by an empirical constant. The derivation then parallels Wilke's[25] treatment of the mixture coefficient of viscosity and results in the following semi-empirical formula:

$$[\lambda^{\circ}_{mix}]_1 \cong \sum_{i=1}^{\nu} \frac{\lambda^{\circ}_i}{1 + \frac{1}{x_i} \sum_{\substack{k=1 \\ k\neq i}}^{\nu} x_k G_{ik}} , \qquad (V.12)$$

where

$$G_{ik} = 1.065\, \phi_{ik} . \qquad (V.13)$$

The factor 1.065 is the value of the empirical constant mentioned above and is the only difference in functional form between $[\lambda^{\circ}_{mix}]_1$ and $[\eta_{mix}]_1$ in eq. (IV.9). Table V-1 shows that, for mixtures of rare gases (Ne-Ar-Kr and He-Ar-Xe), we can obtain excellent agreement with experimental data by using eq.(V.12,13) in conjunction with empirical values of λ°_i. Similar agreement exists for binary mixtures.[14]

We must now consider the correction λ^{int}_{mix} due to the internal degrees of freedom of polyatomic molecules. Hirschfelder[30] has derived the following equation:

$$\lambda^{int}_{mix} = \sum_{i=1}^{\nu} \frac{\lambda_i - \lambda^{\circ}_i}{1 + \frac{\mathcal{D}_{ii}}{x_i} \sum_{\substack{k=1 \\ k\neq i}}^{\nu} \frac{x_k}{\mathcal{D}_{ik}}} , \qquad (V.14)$$

Table V - 1*

Comparison of Theoretical and Experimental Values of Thermal Conductivity Coefficients for Gas Mixtures

GAS MIXTURE	T °K	MOLE FRACTIONS	λ_{mix}(Experimental)** 10^{-5} cal cm^{-1} sec^{-1} K^{-1}		λ_{mix}(Theoretical)[14] 10^{-5} cal cm^{-1} sec^{-1} K^{-1}
H_2-CO_2	273	0.5-0.5	13.50	(44)	13.93 [a]
N_2-CO_2	323	0.5288-0.4712	5.37	(45)	5.22 [a]
	623	0.5288-0.4712	11.27	(46)	10.58 [a]
Ne-Ar-Kr	311	0.1387-0.7172-0.1441	4.50	(47,48)	4.51 [b]
	311	0.5984-0.1301-0.2715	6.58	(47,48)	6.51 [b]
He-Ar-Xe	311	0.1138-0.1495-0.7367	2.84	(49,50)	2.92 [b]
	311	0.6801-0.1880-0.1319	16.62	(49,50)	16.94 [b]
Ar-CH_4-O_2	273	0.751-0.050-0.199	4.59	(51,52)	4.36 [a]
	273	0.677-0.144-0.179	4.91	(51,52)	4.62 [a]
N_2-C_2H_2-O_2	293	0.687-0.141-0.172	5.96	(51,52)	5.77 [a]
	293	0.080-0.900-0.020	5.30	(51,52)	5.23 [a]
	338	0.631-0.211-0.158	6.76	(51,52)	6.52 [a]
	338	0.143-0.821-0.036	6.42	(51,52)	6.25 [a]

* After Mason and Saxena, Reference 14.
** References for experimental data are formed in parentheses.

a. From eq.(V-13,16) of this paper.
b. From eq.(V-12,13) of this paper.

where λ_i is given approximately by eq.(V.7) and eq.(V.8) and is the experimentally determined coefficient of thermal conductivity of a gas consisting only of species i. By using eq.(III.11) in eq. (V.14), we obtain

$$\lambda_{mix}^{int} \cong \sum_{i=1}^{\nu} \frac{\lambda_i - \lambda_i^o}{1 + \frac{1}{x_i} \sum_{\substack{k=1 \\ k \neq i}}^{\nu} x_k \phi_{ik}} . \qquad (V.15)$$

Comparing eq.(V.12), eq.(V.13), and eq.(V.15), we see that only the small difference between G_{ik} and ϕ_{ik} prevents us from combining them in a simple manner. Mason,[14] in fact, substituted G_{ik} for ϕ_{ik} in eq.(V.15) to obtain

$$\lambda_{mix} \cong [\lambda_{mix}^o]_1 + \lambda_{mix}^{int} \cong \sum_{i=1}^{\nu} \frac{\lambda_i}{1 + \frac{1}{x_i} \sum_{\substack{k=1 \\ k \neq i}}^{\nu} x_k G_{ik}} . \qquad (V.16)$$

Table V-1 shows that eq. (V.16), when used with experimentally determined values of λ_i and λ_i^o, is quite accurate. Several authors[13,53,54] have used heuristic arguments rather than the rigorous kinetic theory of gases to derive similar equations.

VI. Thermal Diffusion

The equations for the transport coefficients related to thermal diffusion are more complex and confusing than those discussed in previous sections for the following reasons:

(1) Thermal diffusion is a "second-order" effect, and to evaluate the coefficient of thermal diffusion for species i, denoted D_{Ti}, accurately, we require a Sonine polynomial expansion with more terms than for other transport coefficients.

(2) The coefficients of thermal diffusion are more sensitive to the composition of a gas mixture than are the coefficients representing other transport phenomena.

(3) Because of (1) and (2) above, experiments and theoretical studies have often emphasized binary mixtures, thus impairing our ability to verify the accuracy of formulas for multicomponent mixtures in general.

(4) Three quantities often appear in theoretical work--D_{Ti}, k_{Ti} (thermal diffusion ratio), and α_{ij} (thermal diffusion factor). Authors differ on the definition of D_{Ti} and sometimes (e.g., HCB) fail to show explicitly how the three are related for multicomponent mixtures with $\nu > 2$. CC are also inconsistent in their definitions of k_{Ti} for $\nu = 2$ and $\nu > 2$.

(5) Some of the most authoritative papers on the subject also involve the most complex mathematics and notation, requiring a significant effort for most readers to gain a working knowledge of the equations.

In this section we deal with the above problems in addition to providing a set of useful equations for thermal diffusion coefficients

of multicomponent mixtures. While we use and compare information derived from several sources, we prefer CC because the relationships among $\{D_{Ti}, k_{Ti}, \alpha_{ij}\}$ are stated most clearly and completely. For this reason, we use the notation of CC in this section, rather than the notation of HCB.

A. Thermal Diffusion Coefficients $\{D_{Ti}\}$

The product of $\underset{\sim}{\nabla} \ln T$ and D_{Ti}, the thermal diffusion coefficient for species i in a multicomponent mixture, appears in eq. (A.3) of Appendix A for the diffusion velocity $\underline{V}_i$. Upon reviewing the literature,[55-58] we find that CC, HCB, and Waldman (W) all define D_{Ti} differently. Because we will be more interested in the thermal diffusion ratio, k_{Ti}, which is identical in all three formulations, this subsection will only explore the relationships among D_{Ti}^{HCB}, D_{Ti}^{W}, and D_{Ti}^{CC} rather than giving expressions for evaluating them in terms of properties of a given gas mixture. In the next subsection, we will show how they are related to the set $\{k_{Ti}\}$.

The equations defining the set $\{D_{Ti}\}$ in the three formulations are as follows:

$$\text{CC:} \quad \underline{V}_i = - \sum_{j=1}^{\nu} \Delta_{ij} \underline{d}_j - D_{Ti}^{CC} \underline{\nabla} \ln T \qquad \text{(VI.1a)}$$

$$\text{HCB:} \quad \underline{V}_i = \frac{n^2}{n_i \rho} \sum_{j=1}^{\nu} m_j D_{ij}^{HCB} \underline{d}_j - \frac{1}{\rho_i} D_{Ti}^{HCB} \underline{\nabla} \ln T \qquad \text{(VI.1b)}$$

$$\text{W:} \quad \underline{V}_i = - \sum_{j=1}^{\nu} D_{ij}^{W} \underline{d}_j - D_{Ti}^{W} \underline{\nabla} \ln T \; . \qquad \text{(VI.c)}$$

Eq. (VI.1a-c) show explicitly the relationships of the respective D_{Ti} to the diffusion velocity and multicomponent diffusion coefficients. We readily see that the associated units are $cm^2\ sec^{-1}(D_{Ti}^{CC})$, $g\ cm^{-1}\ sec^{-1}(D_{Ti}^{HCB})$, and $cm^2\ sec^{-1}(D_{Ti}^{W})$. The first term of eq. (VI.1b) differs in sign from those of eq. (VI.1a,c) because the related term in $\phi_i(\underline{r},\ \underline{v}_i,\ t)$ as defined by HCB (see eq. (II.9)) differs in sign from the corresponding term in the other formulations. The quantity Δ_{ij} is a "generalized diffusion coefficient" and is not equal to D_{ij}^{CC}, the multicomponent diffusion coefficient in the formulation of CC, as we show in Appendix F. Waldmann defines his diffusion velocity $\underline{\bar{V}}_i'$, as the velocity of species i relative to the average particle velocity of the mixture,

$$\underline{v}_o' \equiv \sum_i x_i \underline{v}_i, \tag{VI.2}$$

rather than the <u>mass</u> average velocity $\underline{v}_o$; so we have

$$\underline{\bar{V}}_i' \equiv \underline{v}_i - \underline{v}_o' \tag{VI.3}$$

This is the primary distinction between the formulations of CC and Waldmann.[59]

For consistency with eq. (II.21), which constrains the diffusion velocities in the formulations of CC and HCB, and with the equation

$$\sum_{i=1}^{\nu} x_i \underline{\bar{V}}_i' = 0 \tag{VI.4}$$

in the treatment of Waldmann, the respective authors have defined constraint equations for the sets $\{D_{Ti}\}$:

$$\text{CC:} \quad \sum_{i=1}^{\nu} \rho_i \, D_{Ti}^{CC} = 0 \tag{VI.5a}$$

$$\text{HCB:} \quad \sum_{i=1}^{\nu} D_{Ti}^{HCB} = 0 \tag{VI.5b}$$

$$\text{W:} \quad \sum_{i=1}^{\nu} x_i \, D_{Ti}^{W} = 0. \tag{VI.5c}$$

From eq. (VI.1) and (VI.5), we infer that the values of D_{Ti} given by the three formulations are related by

$$\rho_i \, D_{Ti}^{CC} = D_{Ti}^{HCB} = x_i \, D_{Ti}^{W} \tag{VI.6}$$

This will be of use to us in Section VI.B and Appendix F. For completeness, we also list the constraints on the multicomponent diffusion coefficients:

$$\text{CC:} \quad \sum_{j=1}^{\nu} \rho_j \, \Delta_{ij} = \sum_{i=1}^{\nu} \rho_i \, \Delta_{ij} = 0 \tag{VI.7a}$$

$$\text{HCB:} \quad D_{ii}^{HCB} = 0 \tag{VI.7b}$$

$$\text{W:} \quad \sum_{j=1}^{\nu} x_j \, D_{ij}^{W} = \sum_{i=1}^{\nu} x_i \, D_{ij}^{W} = 0. \tag{VI.7c}$$

From eq. (VI.7a-c), we see that the ordinary diffusion coefficients

for multicomponent mixtures are quite different. Fortunately, as we have pointed out in Section III, HCB and CC have derived expressions for the transport coefficients and diffusion velocities in terms of the binary diffusion coefficients $[\mathcal{D}_{ij}]_1$, which are equal in the two treatments.

A general equation for $[D_{Ti}]_1$, the first approximation to the thermal diffusion coefficient for species i, appears in HCB.[60] In the next section, we will show how D_{Ti} may be obtained from the thermal diffusion ratios $\{k_{Ti}\}$.

B. Thermal Diffusion Ratios $\{k_{Ti}\}$ and Thermal Diffusion Factors $\{\alpha_{ij}\}$

Most data from experimental studies of thermal diffusion are presented in terms of the thermal diffusion ratios $\{k_{Ti}\}$, which are unitless. We may understand this emphasis on k_{Ti} by considering eq. (A.4) of Appendix A,

$$\underline{d}_i + k_{Ti} \underline{\nabla} \ln T \cong - \sum_{j=1}^{\nu} \frac{x_i x_j}{[\mathcal{D}_{ij}]_1} (\overline{\underline{V}}_i - \overline{\underline{V}}_j). \qquad (A.4)$$

Usually measurements take place after the gas mixture has reached equilibrium and under conditions in which pressure gradients and external forces are negligible. Eq. (A.4) then becomes

$$\underline{\nabla} x_i + k_{Ti} \underline{\nabla} \ln T = 0, \qquad (VI.8)$$

and k_{Ti} therefore indicates the changes in equilibrium concentration

of species i caused by a temperature gradient in the sample. Because k_{Ti} is so closely related to experimental measurements, we expect that, unlike the situation for the thermal diffusion coefficients $\{D_{Ti}\}$, the treatments of CC, HCB, and Waldmann should provide values of k_{Ti} which are very close or identical. As an example, we show in Appendix F that k_{Ti} is identical in the treatments of binary mixtures given by CC and HCB.

To define the thermal diffusion ratios formally, both CC[61] and Waldmann[57,58] use the same type of equation, i.e.,

$$D_{Ti}^{CC} = \sum_{j=1}^{\nu} \Delta_{ij} \, k_{Tj} \qquad \text{(VI.9)}$$

and

$$D_{Ti}^{W} = \sum_{j=1}^{\nu} D_{ij}^{W} \, k_{Tj} \, , \qquad \text{(VI.10)}$$

respectively. Notice that by using eq. (VI.6) with either eq. (VI.9) or eq. (VI.10), we may calculate the thermal diffusion coefficients in any of the formulations given values for $\{k_{Ti}\}$ and a set of diffusion coefficients. Because the thermal diffusion coefficients are related by eq. (VI.5), we require the auxilliary condition,[62]

$$\sum_{i=1}^{\nu} k_{Ti} = 0 \, , \qquad \text{(VI.11)}$$

to define the set $\{k_{Ti}\}$ unambiguously. The thermal diffusion factors $\{\alpha_{ij}\}$ are defined in terms of the thermal diffusion ratios by the set of equations[57,58,63]

$$k_{Ti} = \sum_{j=1}^{\nu} x_i x_j \alpha_{ij} \qquad (i=1, 2, \cdots, \nu) \qquad \text{(VI.12)}$$

with the auxilliary conditions

$$\alpha_{ij} = - \alpha_{ji} \, . \qquad \text{(VI.13)}$$

CC[41,64] have developed the following useful equation for the first approximation to the thermal diffusion ratio of species i, $[k_{Ti}]_1$, which is based on the assumption that the gases in the mixture are monatomic (or that the internal degrees of freedom are frozen):

$$[k_{Ti}]_1 = \sum_{j=1}^{\nu} \frac{TC_{ij}(x_i a_j m_i - x_j a_i m_j)}{P[\mathcal{D}_{ij}]_1 (m_i + m_j)} \, . \qquad \text{(VI.14)}$$

The quantity C_{ij} is the ratio of collision integrals appearing in eq. (C.10) of Appendix C and a_i is the contribution of the ith species to the mixture thermal conductivity $[\lambda^{\circ}_{mix}]_1$. In Appendix C, we show that

$$a_i \equiv [\lambda^{\circ}_{mix(i)}]_1 \cong \frac{\lambda^{\circ}_i}{1 + \frac{1}{x_i} \sum\limits_{\substack{k=1 \\ k \neq i}}^{\nu} x_k G_{ik}} \, . \qquad \text{(C.1-2)}$$

CC argue that the internal degrees of freedom of the gas molecules have a smaller effect on k_{Ti} than on λ_{mix}. Monchick, et al.[65] add

the condition that the mass and size differences among the species should not both be small. Otherwise, inelastic effects due to non-spherical interactions (e.g., rotational relaxation) must be taken into account. An example of a mixture for which internal degrees of freedom may not be ignored is the D_2-HT system, an "isotopic" mixture, in which both molecular species are approximately the same in mass and size. For such mixtures, Monchick, et al., have derived the corrections to $[k_{Ti}]_1$ due to the internal degrees of freedom of the molecules.

We may convert eq. (VI.14) to a more useful form by using

$$1 + C_{ij} = \frac{6}{5} C^*_{ij}, \tag{C.10}$$

the ideal gas law,

$$P = nkT, \tag{VI.15}$$

and the relationship between $\{m_i\}$ and $\{M_i\}$,

$$\frac{m_i}{m_i + m_j} = \frac{M_i}{M_i + M_j} \quad (i, j = 1, 2, \cdots, \nu). \tag{C.9}$$

We then obtain

$$\begin{aligned} [k_{Ti}]_1 &= \sum_{j=1}^{\nu} \frac{1}{nk[\mathscr{D}_{ij}]_1} \left(\frac{6}{5} C^*_{ij} - 1\right) \frac{x_i x_j M_i M_j}{M_i + M_j} \left(\frac{a_j}{x_j M_j} - \frac{a_i}{x_i M_i}\right) \\ &= \sum_{j=1}^{\nu} x_i x_j \frac{\mu_{ij}(6C^*_{ij} - 5)}{5kn[D_{ij}]_1} \left(\frac{a_j}{x_j M_j} - \frac{a_i}{x_i M_i}\right) \end{aligned} \tag{VI.16}$$

with

$$\mu_{ij} = \frac{M_i M_j}{M_i + M_j} \cdot \qquad \text{(VI.17)}$$

This is the same form of equation derived by Monchick, et al.,[66] for $[k_{Ti}]_1$; however, their equation for a_i includes effects related to internal degrees of freedom and is more complicated from a computational standpoint. Monchick, et al., point out that their result reduces to that of CC for mixtures of monatomic gases. The presence of C^*_{ij}, which is of order unity, increases the complexity of eq. (VI.16). If the reduced temperature range of interest (T^*_A, T^*_B) is small enough, we might simplify our calculations by substituting the average value of C^*_{ij} over (T^*_A, T^*_B) for $C^*_{ij}(T^*)$ in eq.(VI.16) :

$$C^*_{ij} \rightarrow \frac{1}{T^*_B - T^*_A} \int_{T^*_A}^{T^*_B} C^*_{ij}(T^*)\, dT^* \quad . \qquad \text{(VI.18)}$$

For large temperature variations, accurate calculations will require the use of a table of C^*_{ij} values vs. T^* or an accurate fit of a convenient functional form to the tabulated values.

While eq. (VI.15-16) should give an adequate representation of thermal diffusion for reactive flow calculations, we should point out[67] that past calculations of k_T for binary mixtures have not agreed as closely with experimental values as have similar calculations of the other transport coefficients. Thus the reader may require higher-order approximations for other applications.

C. Additional Remarks

Our study has shown that current literature on the theory of thermal diffusion is not uniform in the definition of thermal diffusion coefficients and that treatments of multicomponent mixtures are quite complex. To produce the above discussion of the topic, we have, therefore, often been forced to put together fragmentary information coming from several sources, and our arguments have often been heuristic rather than rigorous. Where possible, we have tested the consistency of the various formulations, and as indicated in Sections A and B and Appendix F, we have found them to be in agreement.

Two theoretical treatments which we have not mentioned are mean-free-path theories[68-72] and the phenomenological approach of van de Ree, et al., based on the thermodynamics of irreversible processes.[73-4] The mean-free-path theories are only qualitatively useful because of the difficulty in computing accurate mean-free-paths related to "number density transfer" and "mean thermal speed transfer." The formulas derived by van de Ree, et al., are equivalent to the treatment of Monchick, et al.,[65,66] in the case of binary mixtures; these equations might thus be of use in detailed studies of thermal diffusion.

VII. Summary of Equations

For ease of reference we summarize the theoretical equations of major interest in evaluating transport properties of multicomponent mixtures of neutral gases. The definitions of the symbols appear in the body of the report on the pages identified in Section VIII "List of Symbols".

A. (Ordinary) Diffusion

1. Self-Diffusion

$$[\mathscr{D}_{ii}]_1 = \frac{0.0026280}{P\sigma_i^2 \Omega_{ii}^{(1,1)*}(T_i^*)} \sqrt{\frac{T^3}{M_i}} \quad (cm^2 sec^{-1}), \tag{III.12}$$

2. Binary Diffusion

$$[\mathscr{D}_{ij}]_1 = \frac{0.0026280}{P\sigma_{ij}^2 \Omega_{ij}^{(1,1)*}(T_{ij}^*)} \sqrt{\frac{T^3(M_i + M_j)}{2 M_i M_j}} \quad (cm^2 sec^{-1}) \tag{III.3}$$

B. Viscosity

1. Pure Gas

$$[\eta_i]_1 = \frac{266.93 \times 10^{-7}}{\sigma_i^2 \Omega_{ii}^{(2,2)*}(T_i^*)} \sqrt{M_i T} \quad (g\ cm^{-1} sec^{-1}) \tag{IV.1}$$

2. Multicomponent Mixtures ($\nu \geq 2$)

$$\eta_{mix} \cong \sum_{i=1}^{\nu} \frac{\eta_i}{1 + \frac{1}{x_i} \sum_{\substack{k=1 \\ k \neq i}}^{\nu} x_k \phi_{ik}} \qquad \text{(IV.9)}$$

$$= \sum_{i=1}^{\nu} \frac{\eta_i}{\sum_{k=1}^{\nu} \frac{x_k}{x_i} \phi_{ik}}$$

$$\phi_{ik} = \frac{1}{2\sqrt{2}} \left(1 + \frac{M_i}{M_k}\right)^{-\frac{1}{2}} \left[1 + \left(\frac{\lambda_i^o}{\lambda_k^o}\right)^{\frac{1}{2}} \left(\frac{M_i}{M_k}\right)^{\frac{1}{4}}\right]^2 \qquad \text{(III.11)}$$

$$= \frac{1}{2\sqrt{2}} \left(1 + \frac{M_i}{M_k}\right)^{-\frac{1}{2}} \left[1 + \left(\frac{\eta_i}{\eta_k}\right)^{\frac{1}{2}} \left(\frac{M_k}{M_i}\right)^{\frac{1}{4}}\right]^2$$

C. Thermal Conductivity

1. Pure Gas

a. Monatomic

$$[\lambda_i^o]_1 = \frac{8.322 \times 10^3}{\sigma_i^2 \, \Omega_{ii}^{(2,2)*}(T_i^*)} \left(\frac{T}{M_i}\right)^{\frac{1}{2}} \text{(erg cm}^{-1} \text{ sec}^{-1} \, ^\circ\text{K}^{-1}\text{)}. \qquad \text{(V.5)}$$

b. Polyatomic

$$\lambda_i = \lambda_i^o + \lambda_i^{int} = \lambda_i^o \, E_i \, . \qquad \text{(V.7)}$$

$$E_i = 0.115 + 0.354 \frac{c_{pi}}{R} \qquad (V.8)$$

$$= 0.115 + 0.354 \frac{\gamma_i}{\gamma_i - 1} ,$$

2. Multicomponent Mixtures ($\nu \geq 2$)

$$\lambda_{mix} \cong [\lambda^{o}_{mix}]_1 + \lambda^{int}_{mix} \cong \sum_{i=1}^{\nu} \frac{\lambda_i}{1 + \frac{1}{x_i} \sum_{\substack{k=1 \\ k \neq i}}^{\nu} x_k G_{ik}} . \qquad (V.16)$$

$$G_{ik} = 1.065 \ \phi_{ik} \qquad (V.13)$$

D. Thermal Diffusion

$$a_i \equiv [\lambda^{o}_{mix(i)}]_1 \cong \frac{\lambda^{o}_i}{1 + \frac{1}{x_i} \sum_{\substack{k=1 \\ k \neq i}}^{\nu} x_k G_{ik}} . \qquad (C.1\text{-}2)$$

$$[k_{Ti}]_1 = \sum_{j=1}^{\nu} \frac{1}{nk\,[\theta_{ij}]_1} \left(\frac{6}{5} C^*_{ij} - 1\right) \frac{x_i x_j M_i M_j}{M_i + M_j} \left(\frac{a_j}{x_j M_j} - \frac{a_i}{x_i M_i}\right) \qquad (VI.16)$$

$$= \sum_{j=1}^{\nu} x_i x_j \frac{\mu_{ij}(6C^*_{ij} - 5)}{5kn[\theta_{ij}]_1} \left(\frac{a_j}{x_j M_j} - \frac{a_i}{x_i M_i}\right)$$

$$\mu_{ij} = \frac{M_i M_j}{M_i + M_j} \qquad (VI.17)$$

VIII. List of Symbols

The following is an alphabetic list of symbols with the number of the page on which each symbol is defined:

(a) $\underline{A}_i$, 6 A_i, 7 A, 10 A', 11 α_o, 20 α_{ij}, 39 a_i, 39 α, 28 α_i, 58 A_{ij}, 63 A^*_{ij}, 65

(b) $\underline{B}_i$, 6 B_i, 7 B_{ij}, 63 B^*_{ij}, 65

(c) $\underline{C}_i^{(j)}$, 6 $C_i^{(j)}$, 7 CC, 3 c_{pi}, 27 c_{vi}, 27 C_{ij}, 39 C^*_{ij}, 40

(d) $\underline{\nabla}$, 1 $\underline{d}_i$, 6 $\mathscr{D}_{ij}^{emp}$, 10 $[\mathscr{D}_{ij}]_1$, 11 $\mathscr{D}_{ii}$, 13 $[\mathscr{D}_{ii}]_1$, 15 D_{ij}, 17 $[D_{ij}]_1$, 17 D_{ij}^{emp}, 18 Δ_{ij}, 34 D_{Ti}, 34 D_{ii}, 36 $\mathscr{D}_{ij}^{\alpha\beta}$, 75 δ_{fi}, 81

(e) E, 2 ε_{ij}, 11 ε_i, 12 η_i, 13 $[\eta_i]_1$, 19 $[\eta_{mix}]_1$, 20 η_{mix}, 23 E_i, 27 ε, 58

(f) f_i, 4 $f_i^{[o]}$, 4 $f_i^{[1]}$, 4

(g) γ_i, 27 G_{ik}, 30 $\underline{G}_i^{\alpha}$, 59 $\underline{g}_i^{\alpha}$, 67 $\underline{g}_i^{-\alpha}$, 70 $\underline{g}_i$, 71 g_{ie}, 78

(h) HCB, 3 H_i^{α}, 58 $\langle H \rangle_i$, 59

(j) J, 4

(k) k, 4 k_{Ti}, 37 $[k_{Ti}]_1$, 39 κ_{mix}, 57

(l) L_i, 1 λ_i^o, 13 λ_{mix}, 25 λ_{mix}^o, 25 λ_{mix}^{int}, 25 λ_{mix}^{comp}, 25 $[\lambda_i^o]_1$, 26 λ_i, 27 λ_i^{int}, 27 $[\lambda_{mix}^o]_1$, 29 $[\lambda_{mix(i)}^o]_1$, 29 L'_{ij}, 63 $|L'|$, 63 L_{ij}, 64 $|L|$, 64

(m) m_i, 4 M_i, 11 μ_{ij}, 41

(n) n_i, 1 ν, 4 n, 6 $\tilde{N}$, 20 η, 26 n_i^{α}, 68

(o) $\Omega_{ij}^{(1,1)^*}$, 11 $\Omega_{ij}^{(1,1)}$, 12 $\Omega_{ij}^{(1)}(1)$, 12 $\Omega_{ij}^{(2,2)^*}$, 19 $\Omega_{ij}^{(2,2)}$, 19 $\Omega_{ij}^{(2)}(2)$, 19

(p) $\underline{P}$, 2 P, 6 ϕ_i, 6 φ_o, 10 Φ_{ij}, 11 Φ_{LJ}, 13 ϕ_{ik}, 13 P_{mix}, 15

(q) Q_i, 1 $\underline{q}$, 2 $\underline{q}^{comp}$, 25 $\underline{q}_i^{int}$, 27 $\underline{q}^{int}$, 69

(r) ρ, 1 $\underline{r}$, 4 ρ_i, 5 r_{ij}, 11 r, 13 R, 20 ρ_i', 21 R_i, 74

(s) $S_n^{(m)}$, 8 s, 10 S, 10 S', 10 s', 11 σ_{ij}, 11 σ_i, 12 σ_i^{α}, 28

(t) t, 1 T, 4 $t_i^{(j)}$, 8 $t_{im}^{(j)}$, 8 T_{ij}^*, 11 T_i^*, 15 T_{mix}, 15 τ_i, 21 $\underline{T}$, 57

(u) $\underline{U}$, 7

(v) $\underline{v}_o$, 1 $\bar{\underline{V}}_i$, 1 $\underline{v}_i$, 4 $\bar{\underline{v}}_i$, 5 $\underline{V}_i$, 6 $\bar{\underline{V}}_i'$, 35 $\underline{v}_o'$, 35 $\bar{\underline{V}}_i^{\alpha}$, 68 $\bar{\underline{v}}_i^{\alpha}$, 68 $\bar{\underline{\mathcal{V}}}_i^{\alpha}$, 70 $\langle \bar{\underline{v}}_i \rangle$, 70

(w) $\underline{W}_i$, 7 W_i, 7 W, 34

(x) $\underline{X}_i$, 4 x_i, 6 x_i^{α}, 68 $\frac{dx_i^{\alpha}}{dz}$, 75 $\left[\frac{dx_i^{\alpha}}{dz}\right]^{int}$, 76 $\left[\frac{dx_i^{\alpha}}{dz}\right]^{comp}$, 76 x_{ie}, 78

(y) Y_{ij}, 82 Y, 82

(z) Z_{ki}, 24

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Appendix A. Transport Properties and the Conservation Equations

Below we summarize and discuss the equations for conservation of mass, particle number, momentum, and energy of multicomponent gas mixtures under the assumption that external forces and radiation processes are neglibible. These equations form the basis for models of reactive flows, and we shall see that the transport phenomena enter the calculations through the conservation equations for particle number, momentum and energy. For detailed derivations, we refer the reader to the treatments of Williams[75] and Landau and Lifshitz.[76]

The "continuity equation" which represents conservation of total mass, is

$$\frac{\partial \rho}{\partial t} + \underline{\nabla} \cdot (\rho \underline{v}_o) = 0 \tag{A.1}$$

The transport coefficients do not appear in Eq. (A.1) because the related transport phenomena do not directly affect the conservation of total mass. However, transport phenomena will affect the conservation equations for mass and particle number of each species i treated separately, since the velocity $\underline{\bar{v}}_i$ may differ from the fluid velocity $\underline{v}_o$. We may express the conservation of particle number for species i as

$$\begin{aligned} \frac{\partial n_i}{\partial t} &= - \underline{\nabla} \cdot (n_i \underline{\bar{v}}_i) + Q_i - L_i n_i \\ &= - \underline{\nabla} \cdot (n_i \underline{v}_o) - \underline{\nabla} \cdot (n_i \underline{\bar{V}}_i) + Q_i - L_i n_i, \end{aligned} \tag{A.2}$$

where Q_i and L_i refer to chemical production and loss processes for species i. In the formulation of HCB,[77] the diffusion velocities $\{\underline{V}_i\}$ are directly related to the coefficients of ordinary diffusion, $\{D_{ij}^{HCB}\}$, and thermal diffusion, $\{D_{Ti}^{HCB}\}$, by the equation

$$\underline{V}_i = \frac{n^2}{n_i \rho} \sum_{j=1}^{\nu} m_j D_{ij}^{HCB} \underline{d}_j - \frac{1}{n_i m_i} D_{Ti}^{HCB} \underline{\nabla} \ln T. \tag{A.3}$$

We have used the superscript "HCB" because other authors define these coefficients differently; Section VI shows the equations of CC and Waldmann which correspond to (A.3). We may also calculate $\{\underline{V}_i\}$ from the set of ν-1 independent equations[78]

$$\underline{d}_i + k_{Ti} \underline{\nabla} \ln T = -\sum_{j=1}^{\nu} \frac{x_i x_j}{D_{ij}^{CC}} (\underline{V}_i - \underline{V}_j) \tag{A.4}$$

$$\cong - \sum_{j=1}^{\nu} \frac{x_i x_j}{[\mathscr{D}_{ij}]_1} (\underline{V}_i - \underline{V}_j)$$

plus Eq. (II.10), which defines $\underline{d}_i$, and Eq. (II.21),

$$\sum_{i=1}^{\nu} n_i m_i \underline{V}_i = 0. \tag{II.21}$$

We discuss k_{Ti}, the thermal diffusion ratio of species i, in Section VI.B. Eq. (A.4) makes use of the fact that each multicomponent diffusion coefficient in the formulation of CC, D_{ij}^{CC}, is approximately equal to $[\mathscr{D}_{ij}]_1$, the first approximation to the binary diffusion coefficient $\mathscr{D}_{ij}$. We have discussed this in Section III.

The equation for conservation of momentum in the absence of external forces is

$$\frac{\partial}{\partial t}(\rho \underline{v}_o) = - \underline{\nabla} \cdot (\rho \underline{v}_o \underline{v}_o) - \underline{\nabla} \cdot \underline{\underline{P}}. \tag{A.5}$$

In Eq. (A.5), the pressure tensor is

$$\underline{\underline{P}} = P\underline{\underline{U}} + \underline{\underline{T}}, \tag{A.6}$$

where $\underline{\underline{U}}$ is the unit tensor and

$$\underline{\underline{T}} = - \eta_{mix}[\underline{\nabla}\underline{v}_o + (\underline{\nabla}\underline{v}_o)^T] + (\frac{2}{3}\eta_{mix} - \kappa_{mix})(\underline{\nabla} \cdot \underline{v}_o)\underline{\underline{U}}. \tag{A.7}$$

In Eq. (A.7), η_{mix} is the coefficient of viscosity of the mixture, $(\ )^T$ is the transpose operation, and κ_{mix} is the "bulk viscosity" coefficient. The bulk viscosity is closely related to relaxation effects between translational motion and the internal degrees of freedom of the molecules and is equal to zero for mixtures of monatomic gases. Williams[75] indicates that κ_{mix} is usually negligible for combustion processes.

The equation for conservation of energy is

$$\frac{\partial E}{\partial t} = - \underline{\nabla} \cdot (E\underline{v}_o) - \underline{\nabla} \cdot (\underline{v}_o \cdot \underline{\underline{P}}) - \underline{\nabla} \cdot \underline{q}, \tag{A.8}$$

where E is the energy density and $\underline{q}$ is the heat flux. The equation defining energy density is

$$E \equiv \frac{1}{2} \rho v_o^2 + \varepsilon, \tag{A.9}$$

in which ε is the internal energy per unit volume. The heat flux, $\underline{q}$, is given by[30,79]

$$\underline{q} = - \lambda^\circ_{mix} \underline{\nabla T} + \sum_{i=1}^{\nu} \sum_{\alpha} \mathcal{N} x_i^\alpha \underline{\bar{V}}_i^\alpha \; H_i^\alpha + \frac{kT}{n} \sum_{i=1}^{\nu} \sum_{j=1}^{\nu} \frac{n_j D_{Ti}^{HCB}}{m_i [\mathscr{D}_{ij}]_1} (\underline{\bar{V}}_i - \underline{\bar{V}}_j). \tag{A.10}$$

In Eq. (A.10), λ°_{mix} is the thermal conductivity of the gas mixture when we ignore the transfer of energy between translational and internal degrees of freedom of the molecules and the effects of chemical reactions. The second term includes the transport of energy by excited quantum states α_i of gas i and also accounts for the transport of heat resulting from changes in chemical composition with temperature. This term is thus directly related to the molecular internal degrees of freedom and to chemical reactions. We have suppressed the index i of α_i for brevity and have used $\mathcal{N}$ to denote total number of moles in the mixture per unit volume. We also point out that Eq. (A.10) treats each quantum state α_i as a separate species; thus $\underline{\bar{V}}_i^\alpha$ is the diffusion velocity of component i in state α_i and H_i^α is the enthalpy per mole of gas i in the quantum state α_i. The last term in Eq. (A.10) represents the "Defour effect" and may be restated in terms of the diffusion ratios $\{k_{Ti}\}$ (see eq. (A.13)).

Appendix D shows how we may separate the second term in Eq. (A.10) into two parts--one which depends on the quantum states $\{\alpha_i\}$ of each component i and the other which depends on the average enthalpy per mole of each component i:

$$\underline{q}_{2nd\ Term} = \underline{q}^{int} + \underline{q}^{comp} \tag{A.11}$$

$$\equiv \sum_{i=1}^{\nu} \sum_{\alpha} \underline{G}_i^{\alpha} H_i^{\alpha} + \sum_{i=1}^{\nu} \mathcal{N} x_i \underline{\bar{V}}_i \langle H_i \rangle .$$

The quantity $\underline{G}_i^{\alpha}$ is the molar flux of component i in quantum state α_i, and $\langle H_i \rangle$ is the enthalpy per mole of component i, averaged over the quantum states $\{\alpha_i\}$. Thus $\langle H_i \rangle$ is the molar enthalpy which we would expect to obtain experimentally for a mixture in equilibrium. Under the conditions listed in Section V.A of this paper, $\underline{q}^{int}$ of Eq. (A.11) becomes

$$\underline{q}^{int} = \sum_{i=1}^{\nu} \sum_{\alpha} \underline{G}_i^{\alpha} H_i^{\alpha} \rightarrow -\lambda_{mix}^{int} \underline{\nabla} T \tag{A.12}$$

where λ_{mix}^{int} then represents a correction to the thermal conductivity of the gas mixture. We derive a useful equation for λ_{mix}^{int} in Section V.B.

The term $\underline{q}^{comp}$ in Eq. (A.11) represents the transport of heat caused by changes in chemical composition with temperature, and under some conditions,[30,80] we may transform $\underline{q}^{comp}$ to a term $-\lambda_{mix}^{comp} \underline{\nabla} T$. Because these conditions include chemical equilibrium at the local temperature T, which does not hold in general, and because the form of $\underline{q}^{comp}$ in Eq. (A.11) is convenient for calculations, we do not attempt to derive λ_{mix}^{comp} in this paper.

By comparing terms in the derivations of $\underline{q}$ given by HCB[81] and CC[82], we find that the Defour effect may be represented by

$$P \sum_{i=1}^{\nu} k_{Ti} \bar{V}_i = \frac{kT}{n} \sum_{i=1}^{\nu} \sum_{j=1}^{\nu} \frac{n_j D_{Ti}^{HCB}}{m_i [\sigma_{ij}]_1} (\bar{V}_i - \bar{V}_j). \qquad (A.13)$$

We may also derive (A.13) by using Eq. (A.4) and Eq. (VI.5) in Eq. (18.31,6) of CC.[82] With Eq. (A.11-13) the heat flux becomes

$$\underline{q} = - (\lambda^{\circ}_{mix} + \lambda^{int}_{mix}) \nabla \underline{T} + \sum_{i=1}^{\nu} n x_i \underline{\bar{V}}_i \langle H_i \rangle + P \sum_{i=1}^{\nu} k_{Ti} \underline{\bar{V}}_i. \qquad (A.14)$$

Appendix B. Sonine Polynomials

Here we use the notation of HCB, defining the Sonine polynomials by the equation

$$S_n^{(m)}(x) = \sum_{j=0}^{m} \frac{(-1)^j (m+n)!}{(n+j)!(m-j)!j!} x^j \tag{B.1}$$

with the orthogonality condition:

$$\int_0^\infty x^n e^{-x} S_n^{(m)}(x) S_n^{(m')}(x) dx = \frac{(n+m)!}{m!} \delta_{mm'} \tag{B.2}$$

If we substitute W_i^2 for x, and use n = 3/2, 5/2, eq. (B.2) gives us

$$\int_0^\infty f_i[0] S_{3/2}^{(m)}(W_i^2) V_i^2 d\underline{V}_i = \frac{3n_i kT}{m_i} \delta_{m0} \tag{B.3}$$

and

$$\int_0^\infty f_i[0] S_{5/2}^{(m)}(W_i^2) V_i^4 d\underline{V}_i = 15 n_i \left(\frac{kT}{m_i}\right)^2 \delta_{m0} \tag{B.4}$$

When we expand A_i and $C_i^{(j)}$ in terms of the set $\{S_{3/2}^{(m)}\}$ and B_i in terms of $\{S_{5/2}^{(m)}\}$ and then substitute these expansions into the integral equations for the transport coefficients, we obtain expressions of the form of eq. (B.3) and (B.4) respectively. For this reason, the Sonine polynomials constitute a convenient choice for calculating approximate values for the transport coefficients.

Appendix C. First Approximations to λ°_{mix}

In this appendix we compare the values of $[\lambda^{\circ}_{mix}]_1$ derived by Mason,[37] Muckenfuss and Curtiss,[39] and CC[41]; we do so to insure that we can derive eq.(V.12) starting with any of these "first approximations" and to indicate how the derivation proceeds. From this we shall see that, in eq.(V.11),

$$[\lambda^{\circ}_{mix(i)}]_1 \cong \frac{\lambda^{\circ}_i}{1 + \frac{1}{x_i} \sum_{\substack{k=1 \\ k\neq i}}^{\nu} x_k G_{ik}} . \quad (C.1)$$

The importance of eq. (C.1) is that we have a simple method of calculating the quantities $[\lambda^{\circ}_{mix(i)}]_1$, which we need in order to compute approximate values of the thermal diffusion ratios (Section VI).

First we must develop equations for $[\lambda^{\circ}_{mix}]_1$ from the formulation of CC[41] which appear in the same form as those of Mason[37] and Muckenfuss and Curtiss.[39]. In the notation of CC, we have

$$a_i \equiv [\lambda^{\circ}_{mix(i)}]_1 \quad (C.2)$$

which are solutions to the set of coupled linear equations,

$$a_i L'_{ii} + \sum_{\substack{j=1 \\ j\neq i}}^{\nu} a_j L'_{ij} = x_i \quad (i=1,2,\ldots,\nu), \quad (C.3)$$

where

$$L'_{ii} = \frac{x_i}{[\lambda_i^o]_1} + \sum_{\substack{k=1 \\ k\neq i}}^{\nu} \frac{Tx_k}{5P[\Omega_{ik}]_1} \frac{6m_i^2 + (5-4B_{ik})\, m_i^2 + 8m_i m_k A_{ik}}{(m_i + m_k)^2}.$$

$$L'_{\substack{ij \\ i\neq j}} = -\frac{x_i T m_i m_j}{5P[\Omega_{ij}]_1} \frac{11-4B_{ij} - 8A_{ij}}{(m_i + m_j)^2}, \qquad (C.4)$$

And A_{ij} and B_{ij} are ratios of collision integrals defined by CC. Next we solve eq.(C.3) by applying Cramer's rule to obtain

$$a_\ell = \frac{\begin{vmatrix} L'_{11} & L'_{12} & \cdots & x_1 & \cdots & L'_{1\nu} \\ L'_{21} & L'_{22} & \cdots & x_2 & \cdots & L'_{2\nu} \\ \vdots & \vdots & & \vdots & & \vdots \\ L'_{\nu 1} & L'_{\nu 2} & & x_\nu & & L'_{\nu\nu} \end{vmatrix}}{|L'|}, \qquad (C.5)$$

(column ℓ)

where $|L'|$ is the determinant of the matrix with elements $\{L'_{ij}\}$. We now multiply the i^{th} columns of the numerator and the denominator, respectively, by $-4x_i$ for each $i = 1,2,\ldots,\nu$ and factor 4 from the ℓ^{th} column of the numerator to obtain

$$a_\ell = 4 \frac{\begin{vmatrix} & & & \text{column } \ell & \\ L_{11} & L_{12} & \cdots & -x_1 x_\ell & \cdots & L_{1\nu} \\ L_{21} & L_{22} & \cdots & -x_2 x_\ell & \cdots & L_{2\nu} \\ \vdots & \vdots & & \vdots & & \vdots \\ L_{\nu 1} & L_{\nu 2} & \cdots & -x_\nu x_\ell & \cdots & L_{\nu\nu} \end{vmatrix}}{|L|} \qquad \text{(C.6)}$$

where $|L|$ is the determinant of the matrix with elements $\{L_{ij}\}$ given by

$$L_{ii} = -\frac{4x_i^2}{[\lambda_i^\circ]_1} - \sum_{\substack{k=1 \\ k\neq i}}^{\nu} \frac{4Tx_i x_k}{5P[\Omega_{ik}]_1} \frac{(11-4B_{ik})m_i^2 + 8m_i m_k A_{ik}}{(m_i + m_k)^2} \qquad \text{(C.7)}$$

and

$$L_{\substack{ij \\ i\neq j}} = \frac{4T}{5P} \frac{x_i x_j}{[\Omega_{ij}]_1} \frac{m_i m_j}{(m_i+m_j)^2} (11 - 4B_{ij} - 8A_{ij}).$$

By eq. (V.11), eq. (C.2), eq. (C.6) and eq. (C.7), we then have

$$[\lambda^\circ_{mix}]_1^{CC} = 4 \frac{\begin{vmatrix} L_{11} & L_{12} & \cdots & L_{1\nu} & x_1 \\ L_{21} & L_{22} & \cdots & L_{2\nu} & x_2 \\ \vdots & \vdots & & \vdots & \vdots \\ L_{\nu 1} & L_{\nu 2} & \cdots & L_{\nu\nu} & x_\nu \\ x_1 & x_2 & \cdots & x_\nu & 0 \end{vmatrix}}{|L|} . \qquad \text{(C.8)}$$

where the notation $[\ ]^{CC}$ identifies the formulation as that of CC. Eq. (C.8) is in the same form as the corresponding equations of Mason and of Muckenfuss and Curtiss[14] the elements $\{L_{ij}\}$ differ, however. To compare the respective sets $\{L_{ij}\}$, we use the following relations in eq. (C.7):

$$\frac{m_i}{m_i+m_j} = \frac{M_i}{M_i+M_j} \quad (i,j = 1, 2, \cdots\cdots, \nu) \qquad (C.9)$$

and [84, 85]

$$A_{ij}^{CC} = \frac{2}{5} A_{ij}^{*HCB} \qquad B_{ij}^{CC} = \frac{3}{5} B_{ij}^{*HCB}$$

$$C_{ij}^{CC\text{-}1953} = 1 + C_{ij}^{CC\text{-}1970} = \frac{6}{5} C_{ij}^{*HCB} \quad . \qquad (C.10)$$

The quantity C_{ij} is another ratio of collision integrals which we encounter in Section VI, and the notations CC-1953 and CC-1970 differentiate between the second and third editions of CC. We then have, from the formulation of CC,

$$L_{ii} = -\frac{4x_i^2}{[\lambda_i^\circ]_1} - \frac{16T}{25P} \sum_{\substack{k=1 \\ k\neq i}}^{\nu} \frac{x_i x_k}{[\Omega_{ik}]_1} \frac{\{(\frac{55}{4} - 3B_{ik}^*)M_i^2 + 4M_i M_k A_{ik}^*\}}{(M_i+M_k)^2}$$

$$L_{\substack{ij \\ i\neq j}} = \frac{16T\, x_i x_j}{25P[\Omega_{ij}]_1} \frac{M_i M_j}{(M_i+M_j)^2}\{\frac{55}{4} - 3B_{ij}^* - 4A_{ij}^*\}. \qquad (C.11)$$

The corresponding equations derived by Mason[37] are

$$L_{ii} = -\frac{4x_i^2}{[\lambda_i^\circ]_1} - \frac{16T}{25P} \sum_{\substack{k=1 \\ k\neq i}}^{\nu} \frac{x_i x_k}{[\Omega_{ik}]_1} \frac{\{\frac{15}{2} M_i^2 + \frac{5}{2} M_k^2 + 4M_i M_k A_{ik}^*\}}{(M_i + M_k)^2}$$

and (C.12)

$$L_{\substack{ij \\ i\neq j}} = \frac{16T}{25P} \frac{x_i x_j}{[\Omega_{ij}]_1} \frac{M_i M_j}{(M_i+M_j)^2} \{10 - 4A_{ij}^*\},$$

and the matrix elements of Muckenfuss and Curtiss[14, 39] are

$$L_{ii} = -\frac{4x_i^2}{[\lambda_i^\circ]_1} - \frac{16T}{25P}\sum_{\substack{k=1\\k\neq i}}^{\nu}\frac{x_i x_k}{[\theta_{ik}]_1}\frac{\{\frac{15}{2}M_i^2 + \frac{25}{4}M_k^2 - 3M_k^2 B_{ik}^* + 4M_i M_k A_{ik}^*\}}{(M_i + M_k)^2}$$

and (C.13)

$$L_{\substack{ij\\i\neq j}} = \frac{16T}{25P}\frac{x_i x_j}{[\theta_{ij}]_1}\frac{M_i M_j}{(M_i+M_j)^2}\{\frac{55}{4} - 3B_{ij}^* - 4A_{ij}^*\} .$$

Notice that the only differences among the three sets of results occur in the bracketed portions concerning the integrals A^* and B^*; in fact, $L_{ij}(i\neq j)$ is the same in eq. (C.11) and eq. (C.13). To derive the approximate expression in eq. (V.12) according to the method of Mason and Saxena,[14] we would set $L_{ij}(i\neq j) = 0$ in eq. (C.11-13). We would then represent the portions of L_{ii} containing M_i, M_k, A_{ik}^*, and B_{ik}^* by an empirical constant. Since the remaining portions of eq. (C.11-13) are identical, all three formulations will lead to the same semi-empirical equation.

Using the above procedure on eq. (C.5), we can see that eq. (C.2) gives

$$[\lambda_{mix(i)}^\circ]_1 = \frac{x_i}{L_{ii}} . \qquad (C.14)$$

Continuing with the treatment of Mason and Saxena,[14] the reader can confirm that eq. (C.1) is correct. As we indicated previously, this is important in calculating the coefficient of thermal diffusion, since we have a simple method of evaluating $[\lambda_{mix(i)}^\circ]_1$, which appears in the approximate expression, eq. (VI.14).

Appendix D. Decoupling the Effects of Molecular Internal Degrees of Freedom and Chemical Reactions in the Heat Flux Equation

In Hirschfelder's treatment of the thermal conductivity of a multicomponent gas mixture[30] (see Section V), he has discussed the heat fluxes $\underline{q}^{int}$ and $\underline{q}^{comp}$, the equations for which depend on the molecular internal degrees of freedom and the chemical composition of the mixture, respectively. In doing so, however, he did not show how to decouple the terms representing these effects in eq. (A.10) for the total heat flux $\underline{q}$. Instead he assumed that eq. (A.11) had already been derived and, therefore, that he could consider each factor independently. Below we show how to derive eq. (A.11) by defining the heat fluxes $\underline{q}^{int}$ and $\underline{q}^{comp}$ in a manner consistent with Hirschfelder's discussion. In Appendix E, we demonstrate that our expressions for $\underline{q}^{int}$ and $\underline{q}^{comp}$ do in fact decouple heat transport caused by changes in the population of quantum states and the chemical composition with temperature, and we show that Hirschfelder's discussions are rigorously valid for chemically reactive mixtures of polyatomic molecules.

Our derivation begins with Eq. (A-10) for the total heat flux $\underline{q}$, which gives us

$$\underline{q} = - \lambda^{\circ}_{mix} \underline{\nabla} T + \sum_{i=1}^{\nu} \sum_{\alpha} \underline{g}_i^{\alpha} H_i^{\alpha} \tag{D.1}$$

in the absence of thermal diffusion. In Eq. (D.1),

$$\underline{g}_i^{\alpha} \equiv \mathcal{N} x_i^{\alpha} \underline{V}_i^{\alpha} \tag{D.2}$$

is the number of moles of component i in quantum state α_i which are moving in 1 sec through a 1 cm^2 surface which is perpendicular to the velocity $\overline{V}_i^{\alpha}$, and H_i^{α} is the enthalpy per mole of component i in quantum state α_i. The quantity $\overline{V}_i^{\alpha}$ is the diffusion velocity of component i in quantum state α_i, given by

$$\overline{V}_i^{\alpha} = \overline{v}_i^{\alpha} - \underline{v}_o, \tag{D.3}$$

and x_i^{α} is the mole fraction of component i in quantum state α_i, given by

$$x_i^{\alpha} = \frac{n_i^{\alpha}}{n} \tag{D.4}$$

with

$$n \equiv \sum_{i=1}^{\nu} \sum_{\alpha} n_i^{\alpha}. \tag{D.5}$$

We have left the index i off α_i in all equations for brevity. Notice also that these and many subsequent equations are restatements of those in Section II assuming that each combination (i, α_i) is a separate component of the mixture. Thus we have for the fluid velocity $\underline{v}_o$ the relation

$$\underline{v}_o = \frac{1}{\sum_{i=1}^{\nu} \sum_{\alpha} n_i^{\alpha} m_i} \sum_{i=1}^{\nu} \sum_{\alpha} n_i^{\alpha} m_i \overline{v}_i^{\alpha}, \tag{D.6}$$

which gives us the equation

$$\sum_{i=1}^{\nu} \sum_{\alpha} n_i^{\alpha} m_i \underline{V}_i^{\alpha} = 0 \tag{D.7}$$

for the diffusion velocities. Since the number of moles per unit volume $\mathcal{n}$ is related to n by

$$\mathcal{n} = \frac{n}{\tilde{N}}, \tag{D.8}$$

where $\tilde{N}$ is Avogadro's number, Eq. (D.7) also represents a constraint on the molar fluxes $\{\underline{g}_i^{\alpha}\}$, i.e.,

$$\begin{aligned} \sum_{i=1}^{\nu} \sum_{\alpha} n_i^{\alpha} m_i \underline{V}_i^{\alpha} &= \sum_{i=1}^{\nu} \sum_{\alpha} \mathcal{n}_i^{\alpha} M_i \underline{V}_i^{\alpha} \\ &= \sum_{i=1}^{\nu} \sum_{\alpha} \underline{g}_i^{\alpha} M_i = 0, \end{aligned} \tag{D.9}$$

where M_i is the molecular weight of component i.

In order to derive Eq. (A.11) from Eq. (A.10), we define $\underline{q}^{int}$ and $\underline{q}^{comp}$ by the equation

$$\underline{q} - \lambda_{mix}^{\circ} \underline{\nabla} T \equiv \underline{q}^{int} + \underline{q}^{comp} \tag{D.10}$$

along with the equations

$$\underline{q}^{int} \equiv \sum_{i=1}^{\nu} \sum_{\alpha} \underline{G}_i^{\alpha} H_i^{\alpha}, \tag{D.11}$$

$$\underline{q}^{comp} \equiv \sum_{i=1}^{\nu} \sum_{\alpha} \underline{g}_i'^{\alpha} H_i^{\alpha}, \tag{D.12}$$

and

$$\underline{g}_i'^{\alpha} \equiv \underline{g}_i^{\alpha} - \underline{G}_i^{\alpha} . \tag{D.13}$$

Next we define the molar flux

$$\underline{G}_i^{\alpha} \equiv \eta x_i^{\alpha} \underline{\bar{v}}_i^{\alpha}, \tag{D.14}$$

where $\underline{\bar{v}}_i^{\alpha}$ is given by

$$\underline{\bar{v}}_i^{\alpha} = \underline{\bar{v}}_i^{\alpha} - \frac{1}{\rho_i} \sum_{\beta} n_i^{\beta} m_i \underline{\bar{v}}_i^{\beta} , \tag{D.15}$$

the average velocity of component i in quantum state α relative to the mass average velocity of component i. From Eq. (II.6) and Eq. (D.15), we obtain

$$\underline{\bar{v}}_i^{\alpha} = \underline{v}_i^{\alpha} - \langle \underline{\bar{v}}_i \rangle , \tag{D.16}$$

where

$$\langle \underline{\bar{v}}_i \rangle \equiv \frac{1}{n_i} \sum_{\beta} n_i^{\beta} \underline{\bar{v}}_i^{\beta} \tag{D.17}$$

with the notation $\langle\ \rangle$ signifying an average over the quantum states of species i. We note that, in equations (D.15) and (D.17), we have used

$$n_i = \sum_{\beta} n_i^{\beta} \tag{D.18}$$

and

$$\rho_i = n_i m_i = \sum_\beta n_i^\beta m_i. \tag{D.19}$$

From Eq. (D.14)-(D.18), we obtain

$$\sum_\alpha \underline{G}_i^\alpha = 0, \tag{D.20}$$

which is the condition used by Hirschfelder[30] to derive λ_{mix}^{int} for a nonreacting gas mixture in a steady state. Thus Eq. (D.11) will give the same formula for λ_{mix}^{int} in the more general case of a reactive gas mixture.

Now we must show that our definition of $\underline{q}^{comp}$ in (D.12) is compatible with Hirschfelder's derivation of the heat flux resulting from changes in chemical composition with temperature. From Eq. (D.2), (D.3), (D.13), and (D.16), we have

$$\underline{g}_i'^\alpha = \mathcal{M} x_i^\alpha [\overline{\underline{v}}_i^\alpha - \underline{v}_o - (\overline{\underline{v}}_i^\alpha - \langle \overline{\underline{v}}_i \rangle)] = \mathcal{M} x_i^\alpha (\langle \overline{\underline{v}}_i \rangle - \underline{v}_o)$$

From Eq. (D.6) and (D.17), we see that

$$\sum_{i=1}^{\nu} n_i m_i (\langle \overline{\underline{v}}_i \rangle - \underline{v}_o) = 0. \tag{D.22}$$

Further the total molar flux of species i in a reference frame moving at the velocity $\overline{\underline{v}}_o$ is given by

$$\underline{g}_i = \sum_\alpha g_i^\alpha = \sum_\alpha (\underline{G}_i^\alpha + \underline{g}_i'^\alpha) = \sum_\alpha \underline{g}_i'^\alpha = \mathcal{M} x_i (\langle \overline{\underline{v}}_i \rangle - \underline{v}_o) \quad . \tag{D.23}$$

From Eq. (II.20) and the accompanying discussion of diffusion velocities $\bar{\underline{V}}_i$, we also have

$$\underline{g}_i = \rho x_i \bar{\underline{V}}_i \tag{D.24}$$

Thus from Eq. (D.22)-(D.24), we obtain

$$\bar{\underline{V}}_i = \langle \bar{\underline{v}}_i \rangle - \underline{v}_o \quad , \tag{D.25}$$

and

$$\underline{g}_i^{\alpha} = \rho x_i^{\alpha} \bar{\underline{V}}_i . \tag{D.26}$$

Using Eq. (D.26) in Eq. (D.12), we find that

$$\begin{aligned} \underline{q}^{comp} &= \sum_{i=1}^{\nu} \sum_{\alpha} \rho x_i^{\alpha} \bar{\underline{V}}_i H_i^{\alpha} \\ &= \sum_{i=1}^{\nu} \rho x_i \bar{\underline{V}}_i \langle H_i \rangle , \end{aligned} \tag{D.27}$$

where as in Eq. (D.17), we have defined $\langle H_i \rangle$ as the enthalpy per mole averaged over the quantum states α_i,

$$\langle H_i \rangle = \frac{1}{x_i} \sum_{\alpha} x_i^{\alpha} H_i^{\alpha} . \tag{D.28}$$

We interpret $\langle H_i \rangle$ as the enthalpy which is measured experimentally; thus Hirschfelder's assumption that the gas is in equilibrium at the local

temperature T is necessary if we use tabulated values of the enthalpy in our models.

Hirschfelder[30] used an equation identical in form to Eq. (D.27) to discuss the effect of changes in chemical composition with temperature upon the thermal conductivity of a gas mixture; again, however, his treatment contains the implicit assumption that the terms associated with molecular internal degrees of freedom will not affect the results. In Appendix E, we outline Hirschfelder's discussion and using the equations which we have developed in this appendix, we show that the above assumption is correct.

Appendix E. Derivation of λ_{mix}^{int} and λ_{mix}^{comp}

Below we outline Hirschfelder's derivation of λ_{mix}^{int} and λ_{mix}^{comp} from $\underline{q}^{int}$ and $\underline{q}^{comp}$, respectively. In our discussion, we will use the more general framework of Appendix D to demonstrate the validity of his treatment. As an example, we will then investigate in detail the case of a gas with only one chemical species.

To simplify our discussion and to parallel Hirschfelder's derivation,[30] we will assume that a temperature gradient exists only along the z-axis, that no heterogeneous reactions take place (i.e., that the bounding surfaces are chemically inert and have no catalytic activity), and that the system has reached a steady state. The last assumption means that

$$\frac{\partial n_i}{\partial t} = 0 \tag{E.1}$$

for each species i, and eq. (A.2) becomes

$$\frac{\partial}{\partial z}\left(n_i[v_o+V_i]\right) = Q_i - L_i n_i. \tag{E.2}$$

Following Hirschfelder, we transform to a local reference frame in which the fluid velocity v_o is zero. We may then express eq. (E.2) in the form

$$\frac{\partial g_i}{\partial z} = R_i, \tag{E.3}$$

where R_i is the net number of moles of component i formed per cm^3 per second. Substituting eq. (D.23) into eq. (E.3), we have

$$\frac{\partial g_i}{\partial z} = \frac{\partial}{\partial z} \sum_{\alpha} g_i^{\alpha} = \frac{\partial}{\partial z} \sum_{\alpha} g_i'^{\alpha} = R_i, \tag{E.4}$$

and we see that only the part of the molar flux which is associated with $\underline{q}^{comp}$ in eq. (D.12) is related to chemical reactions, as we would expect.

To transform eq. (D.11) and (D.12) to expressions of the form

$$\underline{q} = - \lambda \underline{\nabla} T, \tag{E.5}$$

we assume that thermal and pressure diffusion, radiation processes, and external forces are negligible. Under these conditions, eq. (A.4) becomes

$$\frac{dx_i^{\alpha}}{dz} = \sum_{j=1}^{\nu} \sum_{\beta} \frac{x_i^{\alpha} g_j^{\beta} - x_j^{\beta} g_i^{\alpha}}{n \mathscr{D}_{ij}^{\alpha\beta}}, \tag{E.6}$$

in which we distinguish between molecules in different quantum states. We have suppressed the notation $[\ ]_1$ in representing the first approximation to $\mathscr{D}_{ij}^{\alpha\beta}$, the binary diffusion coefficient for component i in state α_i and component j in state β_j. We may now separate the effects of internal degrees of freedom from those of chemical reactions by substituting Eq. (D.13) into Eq. (E.6) to obtain

$$\frac{dx_i^\alpha}{dz} = \left[\frac{dx_i^\alpha}{dz}\right]^{int} + \left[\frac{dx_i^\alpha}{dz}\right]^{comp} \tag{E.7}$$

where

$$\left[\frac{dx_i^\alpha}{dz}\right]^{int} \equiv \sum_{j=1}^{\nu} \sum_{\beta} \frac{x_i^\alpha G_j^\beta - x_j^\beta G_i^\alpha}{\mathcal{N}\mathcal{D}_{ij}^{\alpha\beta}} \tag{E.8}$$

and

$$\left[\frac{dx_i^\alpha}{dz}\right]^{comp} \equiv \sum_{j=1}^{\nu} \sum_{\beta} \frac{x_i^\alpha g_j'^\beta - x_j^\beta g_i'^\alpha}{\mathcal{N}\mathcal{D}_{ij}^{\alpha\beta}} . \tag{E.9}$$

In Eq. (E.8) and (E.9), we have again suppressed the dependence of α_i and β_j on i and j, respectively. Summing Eq. (E.8) over α_i, and referring to Eq. (D.20), we see that

$$\sum_{\alpha} \left[\frac{dx_i^\alpha}{dz}\right]^{int} = 0 \tag{E.10}$$

so that the gradient in chemical composition is given by

$$\frac{dx_i}{dz} = \sum_{\alpha} \left[\frac{dx_i^\alpha}{dz}\right]^{comp} . \tag{E.11}$$

Eq. (E.11) demonstrates the natural decoupling of the effects of internal degrees of freedom and chemical reactions which the framework of Appendix D permits. Performing the sum over α_i in Eq. (E.11) and noting Eq. (D.23), we find that

$$\frac{dx_i}{dz} = \sum_{j=1}^{\nu} \frac{x_i g_j - x_j g_i}{\mathcal{N}\mathcal{D}_{ij}} \qquad (i = 1, 2, \cdots, \nu), \tag{E.12}$$

where we have dropped the dependence of the binary diffusion coefficients on quantum states α_i and β_j following Hirschfelder's assumption.[30] (We have discussed the assumption that $\mathcal{D}_{ij}^{\alpha\beta}$ is independent of α_i and β_j in Section V.A.) If we further assume chemical equilibrium at the local temperature T, Eq. (E.3) becomes

$$R_i(x_1, x_2, \cdots, x_\nu, T, P) = 0, \tag{E.13}$$

from which we may obtain a set $\{x_{ie}(T,P)\}$ describing the equilibrium composition of the system. Hirschfelder[30] indicates that these will provide a first approximation to the actual composition. We may then solve Eq. (E.12) for the set $\{g_i\}$ to obtain[30]

$$g_{ie} = - \left[\frac{\mathfrak{R}^2}{\rho} \sum_{j=1}^{\nu} D_{ij}^{HCB} M_j \frac{dx_{ie}}{dT} \right] \frac{dT}{dz} \tag{E.14}$$

where D_{ij}^{HCB} is a multicomponent diffusion coefficient (formulation of HCB) and the subscript "e" indicates that we have substituted the set $\{x_{ie}(T,P)\}$ into our solution. From Eq. (D.24) and (D.27), we see that

$$q^{comp} = - \lambda_{mix}^{comp} \frac{dT}{dz} \tag{E.15}$$

where

$$\lambda_{mix}^{comp} \cong \frac{\mathfrak{R}^2}{\rho} \sum_{i=1}^{\nu} \sum_{j=1}^{\nu} D_{ij}^{HCB} M_j \langle H_i \rangle \frac{dx_{ie}}{dT} . \tag{E.16}$$

For further discussion of Eq. (E.16), we refer the reader to Hirschfelder[30] and Butler and Brokaw[80].

We now return to Eq. (E.8) to derive an equation analogous to Eq. (E.5) and (E.15) for the thermal conductivity related to internal degrees of freedom. Performing the sum over β and using Eq. (D.4), (D.18), and (D.20), we obtain

$$\left[\frac{dx_i^\alpha}{dz}\right]^{int} = - G_i^\alpha \left(\frac{x_i}{n\mathscr{D}_{ii}} + \sum_{\substack{j=1 \\ j\neq i}}^{\nu} \frac{x_j}{n\mathscr{D}_{ij}} \right), \tag{E.16}$$

in which we have again assumed that the binary diffusion coefficients $\mathscr{D}_{ij}^{\alpha\beta}$ are approximately the same for all α_i and β_j. If each component i is in equilibrium at the local temperature T, the mole fractions x_i^α are functions of local temperature and pressure, and we have

$$\left[\frac{dx_i^\alpha}{dz}\right]^{int} = \left[\frac{dx_i^\alpha}{dT}\right]^{int} \frac{dT}{dz} . \tag{E.17}$$

We may now use Eq. (E.16) and (E.17) in Eq. (D.11) to obtain

$$q^{int} = - \lambda_{mix}^{int} \frac{dT}{dz} \tag{E.18}$$

in which

$$\lambda_{mix}^{int} \equiv \sum_{i=1}^{\nu} \frac{\sum_\alpha \left[\frac{dx_i^\alpha}{dT}\right]^{int} H_i^\alpha}{\frac{x_i}{n\mathscr{D}_{ii}} + \sum_{\substack{j=1 \\ j\neq i}}^{\nu} \frac{x_j}{n\mathscr{D}_{ij}}} . \tag{E.19}$$

To complete the discussion, we will now compute λ^{int} for the case of a gas consisting only of component i. From Eq. (E.19), and the fact that

$$x_j = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases} \tag{E.20}$$

we have

$$\lambda_i^{int} = n\mathscr{D}_{ii} \sum_\alpha \frac{dx_i^\alpha}{dT} H_i^\alpha \, . \tag{E.21}$$

By Eq. (D.28), we know that

$$\langle H_i \rangle = \sum_\alpha x_i^\alpha H_i^\alpha, \tag{E.22}$$

and the molar specific heat at constant pressure for the gas i is

$$c_{pi} = \frac{d\langle H_i \rangle}{dT} = \sum_\alpha x_i^\alpha \frac{d H_i^\alpha}{dT} + \sum_\alpha H_i^\alpha \frac{dx_i^\alpha}{dT} \tag{E.23}$$

The first term is the "translational" contribution to the heat capacity and equals $5R/2$[30]. Thus we find that

$$\lambda_i^{int} = n\mathscr{D}_{ii}(c_{pi} - \tfrac{5}{2} R) \tag{E.24}$$

and the total thermal conductivity for species i becomes

$$\lambda_i = \lambda_i^\circ + n\mathcal{D}_{ii}(c_{pi} - \frac{5}{2}R). \tag{E.25}$$

Defining δ_{fi} by the equation

$$\delta_{fi} = \frac{5R\, n\mathcal{D}_{ii}}{2\lambda_i^\circ} \tag{E.26}$$

we obtain

$$\frac{\lambda_i}{\lambda_i^\circ} = 1 - \delta_{fi} + \frac{2}{5}\delta_{fi}\frac{c_{pi}}{R} \equiv E_i(\delta_{fi}). \tag{E.27}$$

Using detailed calculations with the Buckingham and Lennard-Jones potentials, Hirschfelder[29] has calculated

$$\delta_{fi} = 0.885. \tag{E.28}$$

This gives us the value of E_i shown in Eq. (V.8).

Appendix F. Demonstration that $k_{Ti}^{HCB} = k_{Ti}^{CC}$ for Binary Mixtures

In this appendix, we use the formulation of kinetic theory given by CC to calculate k_{Ti}^{CC} for a binary gas mixture, and we compare the result to the expression for k_{Ti}^{HCB}. We do this to demonstrate the following: that (a) different formulations will give values of k_{Ti} which are equal, (b) Δ_{ij} and D_{ij}^{CC} are not equal, and (c) eq. (VI.6) relating D_{Ti}^{CC}, D_{Ti}^{HCB}, and D_{TI}^{W} is valid. We calculate Δ_{ij} in terms of $\mathscr{D}_{ij}$, which is equal to D_{ij} for binary gas mixtures, from the equation[18]

$$\Delta_{ij} = -\frac{Y_{ij}}{Y} \tag{F.1}$$

where

$$Y = \begin{vmatrix} \frac{x_1^2}{\mathscr{D}_{11}} & \frac{x_1 x_2}{\mathscr{D}_{12}} & \rho_1 \\ \frac{x_1 x_2}{\mathscr{D}_{21}} & \frac{x_2^2}{\mathscr{D}_{22}} & \rho_2 \\ \rho_1 & \rho_2 & 0 \end{vmatrix} \tag{F.2}$$

and Y_{ij} is the cofactor of $\frac{x_i x_j}{\mathscr{D}_{ij}}$ in Q. From eq. (F.1-2) and the equality of $\mathscr{D}_{ij}$ and $\mathscr{D}_{ji}$, we obtain

$$\Delta_{11} = \frac{\rho_2^2}{2\rho_1\rho_2 \frac{x_1 x_2}{\mathscr{D}_{12}} - \rho_1^2 \frac{x_2^2}{\mathscr{D}_{22}} - \rho_2^2 \frac{x_1^2}{\mathscr{D}_{11}}} \tag{F.3}$$

and

$$\Delta_{12} = \frac{-\rho_1\rho_2}{2\rho_1\rho_2 \frac{x_1x_2}{\mathcal{D}_{12}} - \rho_1^2 \frac{x_2^2}{\mathcal{D}_{22}} - \rho_2^2 \frac{x_1^2}{\mathcal{D}_{11}}} . \tag{F.4}$$

CC[18] also state the condition

$$\sum_{j=1}^{\nu} \frac{x_j}{\mathcal{D}_{ij}} = 0, \tag{F.5}$$

which gives us

$$-\frac{x_1}{\mathcal{D}_{11}} = \frac{x_2}{\mathcal{D}_{12}} \quad \text{and} \quad -\frac{x_2}{\mathcal{D}_{22}} = \frac{x_1}{\mathcal{D}_{21}} = \frac{x_1}{\mathcal{D}_{12}} . \tag{F.6}$$

By eq. (VI.9) and eq. (VI.11), we have

$$D_{T1}^{CC} = \Delta_{11}\, k_{T1}^{CC} + \Delta_{12}\, k_{T2}^{CC} = k_{T1}^{CC}\,(\Delta_{11} - \Delta_{12}) \tag{F.7}$$

Using eq. (II.5),

$$\rho = \rho_1 + \rho_2, \tag{F.8}$$

and the above equations, we find that

$$D_{T1}^{CC} = \frac{\rho_2^2 + \rho_1\rho_2}{\frac{x_1x_2}{\mathcal{D}_{12}}(\rho_1+\rho_2)^2}\, k_{T1}^{CC} = \frac{\mathcal{D}_{12}\, k_{T1}^{CC}\, \rho_2}{x_1x_2\rho} . \tag{F.9}$$

We note that eq. (II.6) and eq. (VI.6) give us

$$\rho_1 = n_1m_1, \quad \rho_2 = n_2m_2, \tag{II.6}$$

and

$$\rho_1 \, D_{T1}^{CC} = D_{T1}^{HCB} \quad , \tag{VI.6}$$

Substituting these equations into eq. (F.9), we obtain

$$D_{T1}^{HCB} = \frac{\mathscr{D}_{12} \, k_{T1}^{CC} \, n^2 m_1 m_2}{\rho} \tag{F.10}$$

Solving for k_{T1}^{CC} and comparing this with the corresponding equation[86] for k_{T1}^{HCB}, we find that

$$k_{T1}^{CC} = \frac{D_{T1}^{HCB} \, \rho}{\mathscr{D}_{12} \, n^2 \, m_1 m_2} = k_{T1}^{HCB} . \tag{F.11}$$